RESEARCH

THE BIOLOGY AND CHEMISTRY INVOLVED IN A SILVER-CATALYZED BIOLEACHING PROCESS

Project No. 1-42-487

Final Report

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FINAL REPORT

BY

B. C. RESEARCH COUNCIL

Work on this project was conducted under the auspices of the Canada Centre for Mineral and Energy Technology; Energy, Mines and Resources, Canada.

DSS File Number:	26SQ.23440-3-9002
DSS Contract Serial Number:	QSQ82-00278
CANMET Project Number:	340012
B.C. RESEARCH Project Number:	1-42-487
CANMET Scientific Authority:	Mr. H.W. Parsons

97 pp

March 31, 1984

JUL 9 8 1984

MICROMEDIA

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INTRODUCTION

OBJECTIVES

1. To investigate the chemical and biological aspects of the silver-catalyzed bioleaching of chalcopyrite.

2. To assess the applicability of the process to chalcopyrite and other copper and mixed sulphide concentrates.

3. To investigate the recovery of the silver used as catalyst in the leach process.

BACKGROUND

Studies to develop a microbiological leaching process for coppper sulphide concentrates have been sponsored by industry and government agencies at B.C. Research since 1969. In 1980, a B.C. Research funded project was initiated to continue investigations of a process modification which had been awarded a patent in 1974 (1). This involved the addition of small quantities of silver to the biological leach which resulted in a significant increase in the amount of copper that could be extracted from the mineral chalcopyrite.

In the new study a very important process improvement was made. Not only did the addition of silver improve copper extractions, but, under certain leach conditions, oxidation of the sulphide mineral produced elemental sulphur in the product. Previously, all microbiological leaching reactions resulted in the complete oxidation of sulphide to sulphate. The formation of elemental sulphur in a process conducted at ambient temperatures and at atmospheric pressure was considered a breakthrough in leaching technology. A patent application for the new process has been filed.

In 1982, a new multi company-government agency sponsored program was started with the objective of developing the silver-catalyzed biological leach into a practical process for recovering copper from chalcopyrite concentrates. As a supporting project, a contract was awarded through Supply and Services, Canada to study the biology and chemistry involved in the process. This report presents the findings of this study, performed during the period April 1, 1983 to March 31, 1984.

PERSONNEL

This study was performed in the laboratories of the Division of Extractive Metallurgy, B.C. Research and was carried out by the following personnel:

Dr. R.W. Lawrence	Project Manager
Mr. A. Vizsolyi	Senior Extractive Metallurgist
Mr. R. Vos	Technician
Mr. C. Rule	Technician
Ms. G. Chua	Analytical Technician

ACKNOWLEDGEMENTS

The following organizations have provided financial support to this study: B.P Minerals International Ltd., Cominco Ltd., Henkel Corp., Newmont Mining Corp., Placer Development Ltd., Sumitomo Metal Mining Co. Ltd., Wright Engineers Ltd., B.C. Science Council, and the B.C. Ministry of Energy, Mines and Petroleum Resources. Their support is gratefully acknowledged.

SUMMARY

1. An investigation into the chemistry and biology of the silver-catalyzed biological leaching of chalcopyrite has been carried out.

2. The catalyzed biological leach of chalcopyrite produces a copper-iron leach solution, jarosite and elemental sulphur. Sulphuric acid is consumed. Pyrite is not attacked.

3. The overall reaction stoichiometry for chalcopyrite and bornite has been established.

4. Elemental sulphur formation is ensured through the chemical activation of the mineral by the addition of thiosulphate, silver and cupric ions. Chemical activation is believed to involve the precipitation of a silver-cupric sulphide on the mineral surface. The cupric sulphide is biologically oxidized and replaced by the silver-catalyzed conversion of chalcopyrite in the presence of cupric ions.

5. The role of the bacteria has not been established. It is postulated that biochemical oxidation of sulphide to sulphate does not occur either due to sulphide no longer being incorporated into the cell membrane with elemental sulphur being formed at the mineral surface, or to an inhibition of an enzyme-mediated conversion of polymeric sulphur to sulphate within the cell membrane.

6. The silver-catalyzed bioleach has been run in the continuous mode of operation. Continuous chemical activation was successfully maintained. High copper extraction and

stoichiometric sulphide conversion to elemental sulphur was achieved. The results confirmed the postulated reaction stoichiometry, and that pyrite is not attacked.

7. The applicability of the silver-catalyzed process has been demonstrated for a number of chalcopyrite, bornite and other copper containing mixed sulphide concentrates. The selective leaching of chalcopyrite over pyrite and other minerals is strongly indicated.

8. Recovery of silver catalyst from leach residues is hindered by the presence of jarosite. The bulk of jarosite formation in the leach tank can be prevented by a procedure of solution exchange, allowing the separate formation of a silver-free jarosite. Recovery and recycle of the silver either with the unreacted chalcopyrite and/or following a thiosulphate dissolution step is proposed. Recoveries of 98% have been achieved.

EXPERIMENTAL PROCEDURES

CONCENTRATES

Sulphide concentrates supplied by Newmont Mines Ltd., Gibraltar Mines Ltd., Cominco Ltd., Equity Silver Mines Ltd., Selco Inc., Sumitomo Metal Mining Co. Ltd. and Magma Copper Co. were used in this study.

As required, concentrates were ball milled at 55% solids for 1 hour.

The head assays of the concentrates are listed in Table 1. The probable mineralogical analyses for the concentrates determined on the basis of the elemental analyses and on information provided by the suppliers are shown in Table 2. The size analyses of the as-received and ballmilled concentrates are given in Table 3.

BACTERIAL CULTURES

Cultures of Thiobacillus ferrooxidans for use as inocula in leach tests were maintained in 250 mL Erlenmeyer flasks containing 7.5 or 15 g of concentrate and 75 mL of iron-free nutrient 9K (2). Flasks were incubated at 35° C on a gyratory shaker in a carbon dioxide enriched atmosphere.

BIOLOGICAL LEACH TESTS

Batch Leach Tests

Batch leach tests were performed in baffled plexiglas tanks with a working volume of 2L, equipped with a 4-bladed turbine impeller. Air enriched with carbon dioxide (1%) was introduced under the impeller at a rate of 500 mL per minute. The pH of leach pulps was controlled using a pH meter-controller (Model 45A, Chemtrix Inc.) equipped with a combination pH glass electrode to activate a pump (Masterflex, Cole Parmer Instrument Co.) to deliver 12N sulphuric acid. The Eh of leach pulps was measured using a silver-silver chloride electrode. All leach tests were performed in a controlled temperature room maintained at 33-35° C. Figure 1 shows five of the 2L leach tanks with associated control equipment.

Preparation of Leach Charges

Leach tests conducted under what is termed "standard conditions" were initiated by adding to 1.8 L of iron-free medium 9K to the following components in the order 1.16 g Ag_2SO_4, 142.8 g $CuSO_4.5H_2O$, 12.4 g $Na_2S_2O_3.5H_2O$ and 400 g of copper concentrate. The mixture was conditioned by stirring for 1 to 4 hours before adjusting the pH to the desired initial value, usually 2.2, and adding 75 mL of bacterial inoculum. To eliminate variations in results from a particular series of tests due to differences in bacterial inocula,

large culture volumes were prepared and portions of the same culture added to each individual test. After inoculation, the pH controller was set to deliver sulphuric acid to the leach to maintain the desired operating value.

Continuous Leach Tests

Figure 2 shows a schematic of the set up used for the continuous leach tests.

Concentrate was leached in two plexiglas baffled tanks (A and B) with operating volumes of 1.5 to 3.0 litres. Pulps were agitated and aerated by sparging air containing 1% carbon dioxide at 500 mL/minute under 4-bladed stainless steel turbine impellers (C) driven by Stir-Pak Model K-455800 motors (Cole-Parmer Instrument Co.) (D).

The pH of both leach tanks was controlled using pH meter-controllers (Model 45A, Chemtrix Inc.) (E) equipped with epoxy-bodied combination pH glass electrodes (F) to activate two separate Masterflex pumps (Cole-Parmer) (G) to deliver sulphuric acid from graduated cylinder reservoirs (H). These two pumps were equipped with three pump heads which, in addition to pumping sulphuric acid from individual reservoirs, simultaneously delivered premixed concentrate and copper sulphate from a common agitated tank (I), and a sodium thiosulphate-sulphate solution from another common reservoir (J) to a 200 mL conditioning tank (K) equipped with an axial flow impeller. The conditioned pulp was transferred to the primary leach tank using a continuously operating Masterflex pump (L) to provide overhead suction of the pulp, thereby maintaining a constant operating volume in the conditioning tank. In addition to the two 3-headed pumps, the pH controllers also simultaneously activated Masterflex pumps (M) to transfer pulp from the first to the second leach tank.

At periodic times, pulp was transferred from the second leach tank into a settler (N) of 1 L capacity for separation of the leach products.

The entire system was maintained at 33-35° C in a controlled environment room.

The feed tank contained the Gibraltar concentrate, the corresponding amount of copper sulphate solution to provide the standard copper concentration and the required quantity of 9K nutrient salts. The tank acted only as a mixing reservoir where no chemical or biological activity took place.

Silver-thiosulphate was prepared by dissolving silver sulphate in hot distilled water and, after cooling, slowly adding the solution to sodium thiosulphate solution. In this way, a high thiosulphate concentration prevailed, and the silver was complexed as $Ag(S_2O_3)_3$. The ratio of 0.58 g Ag_2SO_4 to 12.8 g $Na_2S_2O_3.5H_2O$ was used.

The acid demand in Tank #1 activated, through a pH controller, a 3-head pump to simultaneously deliver acid to the leach tank, and chalcopyrite-copper sulphate and silver-thiosulphate to the conditioning tank. Another 3-head pump was provided to deliver acid from Tank #2 acid reservoir to Tank #2, and chalcopyrite-copper sulphate and silver-thiosulphate from the common feed tank and reservoir to the conditioning tank in response to the acid demand in Tank #2.

The 3-head feed pumps were set us so that for each 1 mL of acid delivered to either leach tank, 3.5 mL of concentrate - $CuSO_4$ suspension, and 1 mL of silver-thiosulphate solution were pumped to the conditioning tank. The amounts and strengths of the various reagents added to the feed tanks and reservoirs were adjusted accordingly so that the conditioning tank would contain the standard concentrations of 200 g/L concentrate, 2.8 g $S_2O_3^{2-}$ and 18.2 g/L Cu^{2+}, and 1 g Ag per kg of concentrate (half standard silver addition).

Transfer of conditioned feed to Tank #1 was achieved using continuous overhead suction, thus maintaining a constant volume in the conditioning tank. Since the retention time in the tank was dependent upon both the pulp volume and rate of demand for feed, which in turn was dependent on the acid demand rates, variation in these rates during the test required that the operating volume be adjusted periodically. This was necessary to maintain short retention times for conditioning. The maximum retention time throughout the test was below 4 hours.

Tank #1 was set up initially in batch mode under the standard catalyzed bioleach conditions. During continuous operation, the tank was operated on the principle that as the leach progressed and acid was demanded, the feed constituents would be delivered to the conditioning tank, both feeds being activated by the pH controller set at 2.2. The rise in volume in the conditioning tank caused conditioned feed to be delivered by the level control pump to the leach tank.

When at the start of continuous feeding the volume of pulp in Tank #1 had reached approximately 3 L, 1 L of pulp was transferred to Tank #2. The second 3-head pump was switched on so that the acid demand in the second tank (pH control also at 2.2) would result in the transfer of fresh concentrate and reagents to the conditioning tank. In addition, the Tank 1 to Tank 2 transfer pumps were activated to transfer pulp at a rate equivalent to the feed rate to the primary tank. The pulp from the primary tank was taken at the 2/3 volume level of the tank. Tank #2 operated at a volume between 1.5 L and 2.95 L.

The settler consisted of a 1 L calibrated cylinder with a conical bottom equipped with a stopcock (manually operated). When the pulp volume in Tank #2 was between 2 and 3 L, 1 L of pulp was transferred to the settler for separation and discharge of the leach products.

FLOTATION TESTS

The flotation tests were carried out in a Denver D-12 flotation machine at 1000 RPM, using a stainless steel cell containing 150 g of solid in 1 L of water (13% P.D.). The flotation reagents used were $CuSO_4$ (250 g/tonne), Carboxel D435 (Van Waters) (50 g/tonne) and pine oil (100-200 g/tonne). The pulp pH was 2.8 to 3.0. The pulp was conditioned for 5 minutes and floated for 10 minutes.

SILVER RECOVERY TESTS

Cyanide leach tests were performed by standard bottle roll procedures using standard conditions (pH 11.0, lime, excess cyanide, 24 h retention).

Amonium chloride and ferric chloride/chlorine leaches were performed on desulphurized bioleach residues at 60-70° C.

Thiosulphate leach tests were performed under slightly alkaline conditions (pH 8.0) on both as-obtained and desulphurized residues. Dithionite leach tests were performed in a similar manner but without alkali addition at the natural pH of the system.

ANALYSES

All solid samples were digested first with bromine and then with aqua regia. Copper and iron were determined by atomic absorption spectrophotometry (AA). Total sulphur was determined gravimetrically by the standard barium sulphate method. Elemental sulphur in residues was determined by dissolution in carbon disulphide. Sulphate sulphur in residues was determined by barium sulphate precipitation following

digestion in hydrochloric acid in the presence of a reducing reagent. Silver in solid samples was determined by AA following aqua regia digestion and redissolution in hydrochloric acid (10%). Silver in flotation products was determined by fire assay.

Copper and total iron in leach solutions were measured by AA. Ferrous and ferric iron were distinguished by the sulfosalicylic acid colorimetric method. Sulphate sulphur in leach solutions was determined by the barium sulphate method.

S° PRODUCING LEACH CONDITIONS

INTRODUCTION

Leach tests performed at the start of the experimental program, principally designed to investigate a postulated ferric oxidation mechanism for elemental sulphur production in silver-catalyzed bioleaching, gave inconsistent results. Few leaches produced quantitative conversion of sulphide sulphur to elemental sulphur, while in many tests, conversion was partial or sulphate was the principle sulphur species formed in the reaction products.

It was observed that elemental sulphur formation could be correlated with a low oxidation potential in the leach. At these potentials, ferric iron does not play a role in the chalcopyrite oxidation. The observed low potentials (620-680 mV SHE) can be facilitated by adding sodium thiosulphate. The addition of thiosulphate was also thought to enhance the action of the silver catalyst by forming a soluble silver species. Furthermore, it was found that the addition of soluble copper at the start of the leach, together with the addition of thiosulphate, silver and the bacteria, establishes a set of conditions in which elemental sulphur can consistently be produced. Copper was

added initially because it is a natural component of the system, and also enabled a low potential to be maintained. In addition, at the low potentials achieved through the addition of thiosulphate and copper, it was felt that the cuprous-cupric couple may have a role in mineral oxidation. Sulphuric acid, called in continuously by means of a pH controller to satisfy the requirements of copper and iron dissolution, is also an essential reagent.

The addition of thiosulphate cupric ions and silver at the start of the leach produces chemical reactions which occur before bacterial action is initiated. We have termed these reactions chemical activation.

STANDARD CONDITIONS

The range of effective concentrations for the activation reagents have not been fully established. The concentrations found to be consistently effective for a 20% pulp density (200 g concentrate per L of pulp), referred to as the standard contitions are as follows:

Standard Conditions (20% pulp density):

2.8 g/L $S_2O_3^{2-}$ as $Na_2S_2O_3.5H_2O$
18.2 g/L Cu^{2+} as $CuSO_4.5H_2O$
2 g Ag/kg concentrate as Ag_2SO_4

The lower limits of effectiveness appear to be ~ 2.5 g/L $S_2O_3^{2-}$, ~ 12 g/L Cu^{2+}, and 1 g Ag/kg concentrate.

Experiments in which each of the three reagents copper sulphate, sodium thiosulphate, silver sulphate, and the bacteria were omitted from the leach charge in turn show that all four are essential to consistently produce an elemental sulphur forming reaction. When Newmont concentrate is leached under the standard conditions (all three reagents and bacteria

present), copper extraction is typically > 80%, and quantitative conversion of chalcopyritic sulphur to elemental sulphur is achieved.

When copper sulphate was omitted, the reaction was sulphate producing, and copper extraction from the concentrate was 72%. In the absence of silver, copper extraction was only 25%, the reaction was strongly acid producing and no elemental sulphur was formed. With no thiosulphate added, the final extraction was 80%, and again the reaction was sulphate producing. No copper extraction took place in the absence of bacteria. Similarly, when the bacteria were added, but the reaction was conducted at 50° C, a temperature at which no bacterial growth occurs, no leaching of copper took place.

The oxidation potential of the leach system during elemental sulphur formation is below 680 mV (SHE).

STANDARD CATALYZED BIOLOGICAL LEACH TESTS

NEWMONT CONCENTRATE

The results of a standard leach test performed on Newmont concentrate are shown in Table 4 and Figure 3.

After an induction or activation period of about 40 hours following inoculation, rapid copper leaching took place at a rate of 270 mg/L.h accompanied by a steady sulphuric acid consumption. In Figure 3, copper leached and acid added are plotted on scales with a molar ratio of 1:2, so that a stoichiometric relationship of 2 moles of sulphuric acid added per mole of chalcopyrite oxidized is clearly evident.

When the leach was terminated at 209 hours, 1.53 moles of copper had been extracted (85.2%), and 2.85 moles of elemental sulphur formed, giving a S°:Cu mole ratio of 1.86. 2.55 moles of sulphuric acid were consumed to give a H_2SO_4 consumed:S° produced, and H_2SO_4 consumed:Cu extracted mole ratios of 0.89 and 1.67 respectively.

The final leach solution contained 51.9 g/L Cu and 13.7 g/L Fe at a pH of 2.2. The leach residue weighed 345.7 g and assayed 4.9% Cu, 19.4% Fe, 40.2% S_T and 26.8% S°.

GIBRALTAR CONCENTRATE

The results of leach tests performed under the standard experimental conditions on as-received and ground Gibraltar concentrate are given in Tables 5 and 6, and Figures 4 and 5.

For as-received concentrate, acid consumption started around 30 hours and copper was leached at ~ 250 mg/L.h. Sulphuric acid was called in at a stoichiometrically equivalent rate. According to the material balance, copper extraction was 88.6% at termination. 2.11 moles of S° were produced per mole of Cu leached. The H_2SO_4:S° and H_2SO_4:Cu mole ratios were 0.79 and 1.66 respectively. The final leach solution contained 48.5 g/L Cu and 10.9 g/L Fe. The leach residue weighed 365.6 g and assayed 3.2% Cu, 19.9% Fe, 39.6% S_T and 26.9% S°.

The extraction obtained for ground concentrate was 93.4%, and the copper leach rate was ~ 450 mg/L.h. The effect of grinding the concentrate on leach rate was, therefore, significant. The mole ratios with respect to S°, Cu and H_2SO_4 were similar to those obtained for as-received concentrate. The final solution assay was 53.8 g/L Cu and 11.4 g/L Fe. The leach residue weighed 383.6 g and assayed 1.8% Cu, 21.9% Fe, 36.0% S_T and 25.6% S°.

ANALYSIS OF GIBRALTAR TEST RESULTS

The charge for both Gibraltar leach tests contained 400 g of Gibraltar concentrate and 10 g of Newmont concentrate from the unleached portion in the inoculum, for a total of 410 g. On the basis of head chemical assays, and assuming all copper is present as chalcopyrite, and all non-chalcopyritic iron is present as pyrite, the composition of the charge is calculated to be:

$CuFeS_2$	295.3 g	(= 72.0%)
FeS_2	40.8 g	(= 10.0%)

The fractional analyses of the leach residues were as follows:

	As-Received		Ground	
Cu (in oxidized fraction)	1.27%		1.30%	
Cu (in sulphide fraction)	1.93%		0.44%	
Total Cu		3.2%		1.8%
15e (in oxidized fraction)	13.4%		15.0%	
Fe (in sulphide fraction)	6.5%		6.9%	
Total Fe		19.9%		21.9%
S as S°	26.9%		25.5%	
S as S=	7.8%		5.9%	
S (S° + S=)		34.7%		31.4%
S as SO_4	4.9%		5.4%	
SO_4		14.7%		16.2%
Insol		9.0%		7.7%
TOTAL		81.5%		79.0%

Using the fractional chemical analyses, the probable composition of the unreacted minerals in the residues can be calculated as follows:

		As-Received		Ground	
Weight of Residue		365.6 g		383.6 g	
Cu (as sulphide)		1.93%		0.44%	
corresponds to	Cu	1.93%	7.1 g	0.44%	1.69 g
	Fe	1.69	6.2	0.39	1.48
	S	1.94	7.1	0.44	1.69
	$CuFeS_2$	5.56%	20.4 g	1.27%	4.86 g
Chalcopyrite dissolution	=	(295.3 - 20.4)/295.3		(295.3 - 4.86)/295.3	
	=	93.1%		98.4%	
Fe (as sulphide)		6.52%		6.90%	
Fe (as FeS_2)*		4.8%	17.7 g	4.8%+	18.4 g
corresponds to S		5.5+	20.1	5.5	21.11
FeS_2		10.3%	37.8 g	10.3%	40.0 g
Pyrite attacked	=	(40.8 - 37.8)/40.8		(40.8 - 40.0)/40.8	
	=	7.4%		2.0%	

[* corrected for Fe as $CuFeS_2$]
[+ calculated on basis of FeS_2 formula]

Thus the actual copper extractions of 93.1% and 98.4% for as-received and ground concentrate respectively, are higher than those calculated in the material balances (Tables 5 and 6) and show that some copper is lost to the jarosite in the residue. The calculations also show that only 7.4% and 2.0% of the pyrite was attacked in the as-received and ground concentrates.

The probable composition of the precipitated basic iron sulphate in the residue can be calculated as follows:

	As-Received	Ground
Fe (in oxidized fraction)	13.4% = 0.240 M	15.0% = 0.269 M
SO_4	14.7% = 0.153 M	16.2% = 0.169 M
$Fe:SO_4$	1.57:1	1.59:1

In both cases the $Fe:SO_4$ ratio corresponds to jarosite ($6Fe:4SO_4:12OH$)

OH (calc. on Fe basis)	8.2%	9.1%
TOTAL	36.3%	40.3%

Thus the probable composition of the residues are as follows:

	As-Received	Ground
$CuFeS_2$	5.6%	1.3%
FeS_2	10.3%	10.3%
S°	26.9%	25.5%
Jarosite	36.3%	40.3%
Insol	9.0%	7.7%
TOTAL	88.1%	85.1%

REACTION STOICHIOMETRY

The results of the batch leach tests performed on the Newmont and Gibraltar concentrates have allowed the following reaction stoichiometry to be established for the silver catalyzed biological leach of chalcopyrite:

$$CuFeS_2 + O_2 + 2H_2SO_4 \rightarrow CuSO_4 + FeSO_4 + 2S^\circ + 2H_2O \quad (1)$$

$$FeSO_4 + 1/4\ O_2 + 1/2\ H_2SO_4 \rightarrow 1/2\ Fe_2(SO_4)_3 + 1/2\ H_2O \quad (2)$$

$$1/2\ Fe_2(SO_4)_3 + 7/3\ H_2O \rightarrow 1/3\ H_3Fe_3(OH)_6(SO_4)_2 + 5/6\ H_2SO_4 \quad (3)$$

Thus, the silver-catalyzed reaction consumes acid, and elemental sulphur is produced, contrary to the non-catalyzed, acid producing bioleach. Ferrous iron is oxidized by the bacteria to ferric by reaction (2) and will then hydrolyze to form not only hydronium jarosite as in reaction (3), but a mixture of hydronium, ammonium, potassium, sodium jarosites etc. The acid released by hydrolysis will supplement the acid requirements of reaction (1). The theoretical H_2SO_4 consumption per mole of S° formed is 1.25 [H_2SO_4] (maximum) to 0.83 [H_2SO_4] (minimum), depending on the jarosite composition and quantity.

CONTINUOUS LEACH TEST

INTRODUCTION

It has been shown that in the batch leaching mode, copper extractions of greater than 95% can be achieved from Gibraltar concentrate by the silver catalyzed bioleach. This result was obtained in a leach test characterized by an induction or activation period followed by an extraction period in which copper was leached at rates of ~ 450 mg/L.h. In this period, sulphuric acid was consumed to give an acid to chalcopyrite mol ratio of 2:1. At the end of the leach a final slower extraction rate was observed, with a drop in the acid ratio. Copper dissolution was then accompanied by a more pronounced hydrolytic precipitation.

These experimental results were obtained by mixing, at the start of the leach, silver sulphate/sodium thiosulphate/copper sulphate/9K

nutrients and inoculum in a correct ratio together with the concentrate. This would indicate that a compound (or compounds) was possibly formed on the mineral surface and corresponding decomposition products formed in the solution. If this hypothesis is correct, the key to converting the batch system to continuous operation is to continuously maintain the required chemical reaction at the front end of the process.

The successful conversion from batch to continuous operation proved the validity of this concept and demonstrated that after the initial induction period, the induction period is eliminated, a copper extraction above 80% could be steadily maintained, and a correspondence between sulphuric acid consumed and elemental sulphur produced was in the 90% range.

DATA

The continuous silver-catalyzed leach system was run using reground Gibraltar concentrate for a total time of 850 hours. The data collected daily throughout the run (soluble Cu in tanks, acid consumption and Eh) and values calculated from these and other data (Cu extraction on a solution basis, copper leach rate, copper feed rate, and feed silver concentration) are shown together in Figure 6. The data is also presented on a cumulative basis in Table 7.

The results show that the chemical activation step was successfully maintained at the front end of the circuit, allowing the process to be run in the continuous mode. After an initial induction period associated with the initial batch operation, copper extraction and sulphuric acid consumption were steadily maintained. The copper concentration in solution in tanks 1 and 2 remained quite steady throughout the run at 40-50 g/L and 45-55 g/L respectively. The copper extraction values shown in Figure 6, calculated on the basis of the total copper found in the system daily, represent an average

extraction for the contents of the system at that time, and not the final extraction values for Tank 2 discharge which, as will be shown below, are higher in value.

During the first 550 h of the test, the Eh in tank 1 was, after an initial high period, generally around 430 mV (silver-silver chloride). Most of the copper leaching and acid consumption took place in this tank, and ferric hydrolysis was not extensive. During the same period, tank 2 operated generally above an Eh of 530 mV. In this state, the reactor provided only a small improvement in copper extraction, with substantial ferrous iron oxidation and corresponding ferric hydrolysis. The overall copper leach rate for the two tanks was around 200 mg/L.h.

In the last 300 h of operation, tank 2 was operated at an Eh of around 450 mV, only slightly above that of Tank 1. At this potential, the two tanks performed similarly, and the acid consumption increased twofold with equal consumption in both tanks. Since the feed was directly coupled to the acid demand, the concentrate feed rate was increased correspondingly. The copper leach rate increased significantly with a final steady state value of around 400 mg/L.h. At the termination of the test, the system was operating with a retention time of around 85 h. These latter conditions represent the preferred method of operating the system.

In the early stages of operation, when the Tank 2 Eh was high, a partial gravity separation of the leached solids into two layers occurred in the settler. Initially, the bottom layer which was darker in colour, was pumped back to the primary leach tank for further treatment. After 574 h, no recycle was made, and the two layers were discharged separately and retained. After 717 h, when tank 2 had been operating at a low Eh for about 150 h, a clear distinction of layers in the settler was not evident. All solids were discharged as one component for analyses and further test work.

MATERIAL BALANCES

Table 8 gives the analytical data for the solid products obtained from the settler. Table 9 shows the settler material balance.

Table 10 gives the analytical data for the continuous run material balance in condensed form, taking into account the deportment of the various components in all units of the system at the termination of the run.

Table 11 shows the material balance for the continuous run. Excellent agreement between the throughput quantities and the amounts found in the products was achieved.

From the analyses and overall material balance data for the continuous run, calculations were performed to determine the throughput and meterial balances for copper and sulphur. These calculations are shown in Appendix I.

From the material balance calculations, the results of the continuous run can be summarized as follows:

Cu Extraction	= 12.29 M	= 84.0%
S ($CuFeS_2$) Oxidized		= 80.8%
$S^{=}$($CuFeS_2$) Converted to S°		= 96.7%
S° Formed	= 26.78 M	
H_2SO_4 Consumed	= 24.38 M	

From these data, the mole ratios can be calculated as follows:

[S°]/[Cu]	= 2.18
$[H_2SO_4]/[S°]$	= 0.91
$[H_2SO_4]/[Cu]$	= 1.98

The mole ratios obtained are in agreement with the reaction stoichiometry shown in equations 1 to 3.

COMPOSITION OF CONTINUOUS LEACH RESIDUES

The end products from the continuous run were collected in the settler. As required, the products from the settler were discharged. If separation of layers in the solids was observed, each layer was collected separately. The analytical data for the settler product composites are given in Table 12. The material balance for the settler product composites are given in Table 13.

The analytical and material balance data for the settler product composites was used to calculate the possible composition of the solid leach product. These calculations are shown in Appendix II.

The results of the calculations of the possible leach residue composition is shown graphically and compared with the probable input concentrate composition in Figure 7. These results show that the silver catalyzed bioleach is an effective method for leaching chalcopyrite with the formation of elemental sulphur and jarosite in the solid product. In the 850 h continuous run, where the oxidation of chalcopyrite was in the 80 to 90% range, pyrite decomposition did not occur. The chalcopyrite:pyrite ratio in the feed concentrate was 7.3:1, compared with a ratio of 1:1 in the product.

These conclusions have been reconfirmed by X-ray diffraction data on various leach residues supplied by the Analytical and Assay Branch of the British Columbia Ministry of Energy, Mines and Petroleum Resources. Assays performed on residues taken from leach tests with increasing degrees of oxidation show decreasing quantities of chalcopyrite and relative increasing amounts of pyrite. Jarosite was shown to be formed in the residue.

SUMMARY OF CONTINUOUS LEACH TEST RESULTS

It has been demonstrated that the silver catalyzed bioleach can be run in the continuous mode of operation. The leach system needs to

consist of a reactor in which chemical activation reactions can take place (conditioning tank), and of reactors where, by introducing bacteria, biological activation occurs and oxidation (leaching) takes place.

The copper leach rate reached a steady state of ~ 400 mg/L.h when two leach tanks were performing at a low oxidation potential and at a similar level of activity. The retention time under these conditions was around 85h. Copper extractions above 80% were achieved.

The final products of the leach correspond to the production of a copper-iron leach solution, elemental sulphur and jarosite from the decomposition of chalcopyrite. The previously established reaction stoichiometry for batch leaches was verified for the continuous mode of operation.

BIOLOGICAL AND CHEMICAL PHENOMENA

POSTULATED BIOLOGICAL MECHANISMS

We do not currently have the capability to conduct investigations into the biological and biochemical aspects of the silver catalyzed bioleach process. However, based on the results obtained and observations made during the program, some postulations can be made about what is happening biologically during the catalyzed bioleach and comparisons made with conventional, or uncatalyzed, bioleaching.

Conventional Bioleaching

Uncatalyzed or conventional bioleaching of chalcopyrite can be represented by the following reaction:

$$4CuFeS_2 + 17O_2 + 4H^+ \rightarrow 4Cu^{2+} + 4Fe^{3+} + 8SO_4^{2-} + 2H_2O \qquad (4)$$

Sulphide sulphur is oxidized completely to sulphate and ferrous iron is oxidized to ferric. In the pH range favoured by the bacteria (~ 2), ferric iron tends to hydrolyze and precipitate as jarosite, releasing acid.

$$3Fe^{3+} + 2SO_4^{2-} + 7H_2O \rightarrow H_3OFe_3(SO_4)_2(OH)_6 + 5H^+ \qquad (5)$$

Thus the overall reaction (the sum of equations 4 and 5) is a net acid producer.

Reaction (4) can be broken down into its respective anodic and cathodic reactions as follows:

Anodic

$$CuFeS_2 + 8H_2O \rightarrow Cu^{2+} + Fe^{3+} + 2SO_4^{2-} + 16H^+ + 17e^- \qquad (4a)$$

Cathodic

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad (4b)$$

With most mineral sulphide oxidation reactions, reduction of the oxidant is rate controlling rather than oxidation of the mineral (3).

It has been shown (4) that T. ferrooxidans can attach directly to the sulphide mineral, with sulphide oxidation proceeding via two enzyme-mediated stages. In the first stage, sulphide loses two electrons and polymerization of the resulting sulphur atoms occurs. The polymeric sulphur compounds are then oxidized to sulphate, with thiosulphate and/or sulphite being intermediate products. These processes are thought to occur in the cell membrane. The electrons generated by oxidation are transferred via the cytochrome transport chain of the cell to their ultimate acceptor, molecular oxygen. Thus, the bacteria ultimately act to facilitate reduction of oxygen, the rate determining step.

Catalyzed Bioleaching

Catalyzed bioleaching of chalcopyrite, an acid-consuming, sulphur producing reaction, can be represented as follows:

$$4CuFeS_2 + 5O_2 + 2OH^+ \rightarrow 4Cu^{2+} + 4Fe^{3+} + 8S^\circ + 10H_2O \qquad (6)$$

Comparing equation (6) to equation (4), it can be seen that conventional bioleaching requires 4 1/4 moles oxygen per mole chalcopyrite, whereas catalyzed bioleaching requires only 1 1/4 moles oxygen per mole.

Reaction (6) can be broken down into its respective anodic and cathodic reactions as follows:

Anodic

$$CuFeS_2 \rightarrow Cu^{2+} + Fe^{3+} + 2S^\circ + 5e^- \qquad (6a)$$

Cathodic

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad (6b)$$

Note that the cathodic reaction, the reduction of oxygen, for catalyzed bioleaching is the same as that for conventional bioleaching. Since the oxygen requirement per mole of chalcopyrite for catalyzed bioleaching is less than that of conventional leaching, copper leach rates could be expected to be higher. However, the anodic reaction involves oxidation of sulphide to sulphur rather than to sulphate, a process which provides a reduction in electron transfer, and hence a reduction in metabolic energy available for bacterial growth, equivalent in magnitude to the reduction in oxygen requirement. This would explain the much lower bacterial popluations observed during catalyzed bioleaching. Leach rates could be expected to be at least as high as conventional bioleaching. The experimental observations presented in this report support this postulation.

For reasons that are not clearly understood, the use of copper sulphate, thiosulphate and silver produces a condition in which biochemical oxidation of sulphide to sulphate does not occur. Ferrous oxidation to ferric is not affected. The overall mechanisms may have been altered in one of two ways:

1) Sulphide is no longer incorporated into the bacterial cell membrane, with elemental sulphur now forming at the mineral surface. Electron transport through the bacteria is not effected.

2) Sulphide is incorporated into the cell membrane and proceeds through the first stage of oxidation, but then stops due to inhibition of the second-stage enzyme-mediated oxidation reaction (polymeric sulphur to sulphate). In this case elemental sulphur is formed in the cell membrane.

In either case, the imposition of a lower redox potential, caused by the addition of copper sulphate and thiosulphate, appears to result in sulphur being a more thermodynamically favourable product than sulphate.

POSSIBLE CHEMICAL REACTIONS INVOLVED IN THE PROCESS

Silver and cuprous copper form identical complexes with thiosulphate ions. The stability constants for the silver thiosulphate ($\log K_1$ = 8.82; $\log K_2$ = 13.5), and for cuprous thiosulphate ($\log K_1$ = 10.3; $\log K_2$ = 12.2; $\log K_3$ = 13.8) indicate almost equal strength in stepwise formation or decomposition.

In the chemical activation procedure a silver-thiosulphate solution is prepared in which thiosulphate is in large excess. Thus all the silver is complexed and additional, uncomplexed thiosulphate is present. The copper sulphate solution, with a high cupric content, is

introduced with the concentrate as a slurry together with the silver-thiosulphate solution, into a conditioning vessel. In the conditioner, cupric reacts with the thiosulphate forming cuprous thiosulphate and corresponding tetrathionate. Through further possible interactions, the final decomposition products will be cuprous and cupric sulphide and sulphuric acid. This concept can be illustrated by the following equations:

$$Cu^{2+} + S_2O_3^{2-} \rightarrow Cu^{+} + 1/2S_4O_6^{2-} \quad (7)$$

$$2Cu^{+} + S_2O_3^{2-} \rightarrow Cu_2S_2O_3 \quad (8)$$

and

$$Cu_2S_2O_3 + H_2O \rightarrow Cu_2S + H_2SO_4 \quad (9)$$

Similarily,

$$Ag_2S_2O_3 + H_2O \rightarrow Ag_2S + H_2SO_4 \quad (10)$$

These equations only represent the overall final reactions and do not take into account the many intermediate compounds that may form (cupric trithionate, polythionates, etc.) and the decomposition reactions of cuprous thiosulphate into Cu_2S and CuS instead of Cu_2S only.

Therefore as cuprous thiosulphate is formed, the excess thiosulphate protecting the silver thiosulphate complex is used up, and through the demasking, the final precipitation of silver sulphide/cuprous and cupric sulphide occurs. These sulphides act as a mixture or as a compound as the active participant in the chalcopyrite decomposition reactions.

In the suggested mechanism, as soon as the cuprous and cupric sulphides are oxidized, with corresponding acid call-in and elemental sulphur production, the chalcopyrite dissolves to replace the copper sulphide and re-establish the equilibrium. As suggested (5), Cu_2S first reacts to form CuS as follows:

$$Cu_2S + HSO_4^- + 7H^+ + 6e^- \rightarrow 2CuS + 4H_2O \quad (11)$$

and,

$$HSO_4^- + 7H^+ + 6e^- \rightarrow S^\circ + 4H_2O \quad (12)$$

resulting in the net reaction

$$Cu_2S + S^\circ \rightarrow 2CuS \quad (13)$$

In our postulation CuS is oxidized as follows:

$$CuS + O + 2H^+ \rightarrow Cu^{2+} + H_2O + S^\circ \quad (14)$$

Then, equilibrium is re-established by:

$$CuFeS_2 + Cu^{2+} \rightarrow 2CuS + Fe^{2+} \quad (15)$$

The silver sulphide acts as a catalyst in that it mediates the chalcopyrite decomposition as it takes up and releases the cuprous and/or cupric sulphides.

These postulations are supported by the following experimental observations:

1. In all experiments the pH at the start drops due to acid formation and corresponding sulphide precipitation.

2. Compounds isolated from leach tests and from synthetic solutions contained silver, copper and sulphide with the composition 58% Cu, 12.5% Ag and 21% S corresponding to a Ag_2S - 10 $Cu_{1.5}S$ mixture, or to a $Ag_{0.18}Cu_{1.4}S$ compound.

3. It has been found that if a separation of the solid leach charge is made after the conditioning stage and the solids resuspended in 9K medium alone and inoculated, then a conventional, acid producing bioleach takes place in the same way as would the original BCR silver catalzyed, sulphate producing process (1). If, however, pretreated solids are resuspended in a copper sulphate - thiosulphate system, the reaction will be elemental sulphur producing. Therefore the solution, with respect to the high Cu^{2+} concentration, the possible various thiosulphate and thionates compositions, and the resulting low Eh, is responsible for the sulphur producing mechanism.

   The above postulated reaction mechanism is probably only valid at low potentials. When the potential rises towards the end of the leach and the ferric concentration increases, a ferric oxidation mechanism could apply.

APPLICABILITY OF CATALYZED BIOLEACH PROCESS TO ADDITIONAL SULPHIDE CONCENTRATES

INTRODUCTION

The possibility of producing elemental sulphur during the catalyzed biological leaching of chalcopyrite has been demonstrated by results of leach tests on Newmont and Gibraltar concentrates. This section presents the results of tests performed to determine the applicability of the catalyzed leach to additional concentrates. These concentrates contain, in addition to the predominant chalcopyrite, other copper minerals such as tetrahedrite, tennantite and enargite, and numerous non-copper minerals in major and minor amounts.

With the lack of mineralogical analysis of leach residues, we have not been able to establish through chemical analysis, conclusively in all

cases, that minor amounts of copper minerals in addition to the major chalcopyrite are responsive to the sulphur producing process. In other cases, notably with bornite, a favourable response has been established.

What has also been established is that the presence of minerals in addition to chalcopyrite does not appear to interfere with the process on chalcopyrite (or bornite). Whether or not these minerals are involved in the reactions cannot be assessed.

The various concentrates investigated are listed with their corresponding head assays and estimated mineralogical compositions in Tables 1 and 2 respectively.

WHITEHORSE CONCENTRATE

The Whitehorse concentrate, obtained from Cominco, is a bornitic type containing some vallerite, and small amounts of covellite, chalcocite and cuprite.

Leach tests performed under the standard leach conditions on this concentrate had very long induction (lag) times, the duration of which correspond to the rate of sulphuric acid uptake for neutralization (Figure 8).

The use of bacterial cultures extensively sub-cultured on the Whitehorse concentrate did not produce any reduction in the length of the induction period. The results of an experiment to determine whether a separate acid pretreatment before the start of the bioleach would reduce the lag time are shown in Figure 9. The acid pretreatment, consisting of treating 400 g of concentrate for 15 h at 60° C resulted in a net acid uptake of 100 mL of 12N sulphuric acid and a copper dissolution of 8.8 g/L. After pretreatment, the cooled charge was subjected to the standard Ag-thiosulphate, 9K nutrient and inoculum addition for a catalyzed bioleach.

The effect of the pretreatment was to considerably reduce the length of the induction period. Without pretreatment, 80.3% Cu was extracted, equivalent to 150.0 g Cu. Of this amount, 125.2 g was extracted by the biological process, and a corresponding 72 g of S° was produced, equivalent to 95% of the theoretical 5:6 mol ratio of sulphuric acid exchange for elemental sulphur production for bornite leaching (see below). The copper leach rate was 280 mg/L.h.

The leach of acid pretreated concentrate achieved 95.2% copper extraction, and produced a residue assaying 3.5% Cu and 17.0% S. 501 mL of sulphuric acid was consumed, including 100 mL for the pretreatment. The corresponding S°/Cu, H_2SO_4/S° and H_2SO_4/Cu mol ratios were 0.75, 1.41 and 1.07 respectively.

With or without pretreatment, the start of bioleaching is marked by rapid dissolution of copper, coupled with a corresponding amount of sulphuric acid consumption and sulphur production. The reactions can be represented as follows:

$$Cu_5FeS_4 + 3O_2 + 6H_2SO_4 \rightarrow 5CuSO_4 + FeSO_4 + 4S^\circ + 6H_2O \quad (16)$$

$$FeSO_4 + 1/2O_2 + 1/2H_2SO_4 \rightarrow 1/2Fe_2(SO_4)_3 + 1/2H_2O \quad (17)$$

$$1/2Fe_2(SO_4)_3 + 2H_2O \rightarrow 1/6H_2Fe_6(OH)_{12}(SO_4)_4 + 5/6\ H_2SO_4 \quad (18)$$

If no hydrolysis takes place, this would represent a 5[Cu] to 6[H_2SO_4] mol correspondence. If jarosite formation is prevalent, the mol ratio would be 5 to 5.66. The observed mol ratio obtained in the experiment on pretreated concentrate (Figure 10) very much suggests that the above stoichiometry is correct. This is also clearly demonstrated in Figures 8 and 9 in which the copper leached and acid added are plotted on scales with a mole ratio of 5[Cu]:6[H_2SO_4].

EQUITY CONCENTRATE

The Equity concentrate provided by Placer Development Ltd. was a silver rich pyritic concentrate containing a low percentage of chalcopyrite. The concentrate contained ~ 6% Cu, representing a maximum chalcopyrite component of ~ 17%. Some minor amounts of tetrahedrite, tennantite and arsenopyrite are also likely present. This concentrate is of interest because of the possibility of treating middling types of flotation product to extract its copper value.

The results of experiments performed under standard conditions, with no silver, with 1/2 silver, and again under standard conditions are given in Tables 14 to 17.

Copper extractions obtained in the four tests were in the range 70-85%. The result of the test under standard conditions (Table 14) shows that the copper (chalcopyrite) was extracted preferentially to the other components. Little of the high pyrite content, or the arsenic, antiomny and bismuth were leached. It is thought unlikely that these minor mineral components were actually oxidized and their products subsequently converted to an insoluble salt.

It can be seen that there is apparently a low sulphuric acid consumption in these tests as reflected by the low $H_2SO_4/S°$ and H_2SO_4/Cu mol ratios. For example, under standard conditions (Table 14), ratios of 0.39 and 1.03 respectively were obtained. Theoretically, values closer to 1.0 and 2.0 would be expected (for chalcopyrite). However, it must be seen that this concentrate is predominantly pyrite with only a relatively small amount of chalcopyrite. A calculation based on the head assay indicates a pyrite content of around 50%. It can be further calculated that oxidation of anly a small fraction of the pyrite (~ 10%) would generate sufficient acid which, if added to the quantity demanded by the chalcopyrite oxidation, would result in the mol ratios being closer to their theoretical values.

The test series with standard, half or no silver addition (Tables 15 to 17) shows that this concentrate does not need a silver addition to allow the sulphur producing reaction to take place. This could be a result of the high silver content (0.137%) of the concentrate, some of which in the presence of thiosulphate, may become available for reaction. Alternatively, the precipitation of copper sulphides only from the decomposition of the copper-thiosulphate may have been sufficient to carry the reaction to ~ 80% completion.

SELBAIE CONCENTRATE

The Selbaie concentrate, obtained from Selco Inc. (B.P.), was interesting because it contains chalcopyrite with sphalerite. The results of test work performed on this concentrate are presented in Figures 11 and 12, and Table 18.

The concentrate leached similarly and as easily as other chalcopyrites in a standard test. A copper extraction of 92.5% (1.63 M) and a copper leach rate of 295 mg/L.h were obtained (Figure 11). Zinc was leached simultaneously to 81.1% extraction (0.48 M). The parallel copper and zinc dissolution is shown more clearly on a mol fraction leached basis in Figure 12. 3.04 moles of elemental sulphur were produced.

It is believed that only chalcopyrite was oxidized with corresponding formation of elemental sulphur, and that zinc sulphide was leached through oxidation to sulphate. This conclusion is based on both the acid consumption and the elemental sulphur production values. These correspond well to the amount of copper leached, as can be seen from the S°/Cu, H_2SO_4/S° and H_2SO_4/Cu mol ratios of 1.87, 0.84 and 1.57 respectively. If the amount of zinc leached (0.48 M) is included in these ratios, their value would be substantially lower than theoretical ($S^{\circ}/Cu + Zn$ mol ratio = 1.44, $H_2SO_4/Cu + Zn$ = 1.21).

SUMITOMO CONCENTRATES

Two concentrates, designated C and P, were received from Sumitomo Metal Mining Co. Concentrate C contans the copper minerals chalcopyrite, enargite and tetrahedrite-tennantite, with pyrite. Concentrate P contains mainly pyrite with copper occurring as enargite (luzonite) and djurleite.

Only one leach test was performed on the small amount received of concentrate P. This test was not successful in achieving a sulphur producing leach. Pyrite was apparently oxidized with a corresponding production of sulphuric acid.

Concentrate C was leached under the standard conditions both as-received and ballmilled. A ballmilled sample was also acid pretreated for 5 h at 70° C prior to bioleaching. A silver addition of half the standard amount was also evaluated for a ballmilled sample. The results of these tests are shown in Figures 13 to 15, and in Table 19.

Concentrate C responded well to the process with copper extraction values in the range 86-94% being achieved. Copper leach rates were in the range 250 mg/L.h for as-received concentrate to 650 mg/L.h for acid pretreated, ball-milled concentrate.

MAGMA CONCENTRATE

This chalcopyrite concentrate was received from the Magma Copper Co. through Newmont Mining Corporation.

The results of a leach test performed under the standard conditions are given in Figure 16. Following a long induction phase, a fast copper leach rate of 440 mg/L.h was achieved. The leach residue weighed 336.6 g and assayed 1.86% Cu and 21.29% S°. The copper

extraction on a residue basis is therefore 94.5%. 338 mL of 12 N H_2SO_4 were consumed. The S°/Cu, H_2SO_4/S° and H_2SO_4/Cu mol ratios were calculated to be 1.32, 0.91 and 1.20 respectively.

CONCLUSION

Investigations of the silver catalyzed bioleach process have been extended to tests on the following concentrates: Whitehorse, Equity, Selbai, Sumitomo C, Sumitomo P and Magma. With the exception of Sumitomo P (enargite), all concentrates responded favourable to the process. The results have confirmed that high extraction and leach rates can be obtained for chalcopyrite. The selectivity of chalcopyrite leaching over other sulphides is strongly indicated. The applicability to treat bornite has also been established. With the Selbaie concentrate, both chalcopyrite and sphalerite were leached simultaneously, although it is thought that sphalerite was oxidized to produce sulphate.

RECOVERY AND RECYCLE OF SILVER CATALYST

The recovery of silver added as catalyst from the leach products for recycle, together with precious metals originally present in the concentrate, is required for the overall viability of a catalyzed biological leaching process. This section discusses the form and deportment of silver in the leach products and presents the results of recovery studies performed to date.

The aqueous acid oxidation of copper-iron-sulphide minerals (chalcopyrite, bornite) results in the solubilization of copper and iron. The iron first dissolves as ferrous but is further oxidized to ferric which then hydrolyzes with the formation of a basic ferric salt.

In pressure oxidation, the end product of hydrolyses could be jarosite, ferric hydroxide, goethite or hematite depending on pH and temperature. In biological leaching the requirements for bacterial activity limit the pH range to ~ 20° to 35° C. These limits define the stability range of jarosite assemblages (6).

In most of the process flowsheet options being considered and evaluated, a flotation step is used to separate unreacted chalcopyrite and elemental sulphur from pyrite, jarosite and gangue material. The results of a flotation test performed on a composite leach residue produced during the continuous leach test are shown in Table 20. The results indicate that flotation achieves high copper and sulphur recovery together with about 60% of the silver. Thus, further treatment of the flotation tails would be necessary to recover the remaining silver catalyst and precious metals from the jarosite. The form of the silver is probably as silver jarosite, or as insoluble silver compounds (chloride, phosphate, arsenate, etc.) included in the jarosite.

The jarosite produced at low temperature and at atmospheric pressure in the biological leach is very reactive both in dissolution in acid:

$$2HFe_3(OH)_6(SO_4)_2 + 5H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2H_2O \qquad (19)$$

or by conversion with alkali:

$$HFe_3(OH)_6(SO_4)_2 + 4NaOH \rightarrow 3Fe(OH)_3 + 2Na_2SO_4 + H_2O \qquad (20)$$

Treatment of residues by thiosulphate to recover silver does not seem to be affected by the formed jarosite. The use of thiosulphate is desirable since silver would be recovered in a form suitable for direct recycle to the activation stage of the leach circuit. However, thiosulphate leaching is only adequate to recover around 80% of the added silver. Thus, further treatment by, for example, cyanidation is necessary before the tail is discarded.

An acid treatment to redissolve jarosite could be used to prepare a jarosite free residue for standard cyanidation. However, large quantities of acid and corresponding alkali would be required for dissolution and reprecipitation of a purified jarosite for disposal.

If direct cyanidation of residue is attempted, all the jarosite would need to be converted and an excessively high alkali consumption would result (equation 20) before the cyanidation pH could be reached. Furthermore, excessive cyanide consumption would be experienced since the jarosite impurities (Cu, Zn, etc.) would now be present as hydroxide which are cyanicides.

Cyanide leach tests performed on residues only achieved a maximum of 60% silver recovery. The use of chloride to leach silver only achieved 45-55% recoveries. The chloride system would also be subject to excessive acid consumptions.

The problems involved with the presence of jarosite in the biological leach residues allowed the development of a unique possiblity in silver recovery. In the biological system operated at a low potential and below 35° C, iron is present predominantly in the ferrous form, and ferric iron present has not yet been hydrolyzed. The leached iron can be removed by decantation or filtration to be oxidized and hydrolyzed in a separate system. The oxydrolysis can be achieved by biological or chemical oxidation, and hydrolysis effected by temperature, and if necessary pH, adjustment. The removed solution does not contain silver so that a silver-free jarosite is precipitated. The low-iron copper solution is then recirculated.

Thus the bulk of the jarosite is processed separately and does not contain silver. Insoluble silver compound oxidation products will remain with the unoxidized silver catalyst (sulphide) on the unreacted chalcopyrite. Thus, the silver may be recycled with the unreacted chalcopyrite, or be available for high recovery dissolution in thiosulphate.

In evaluating the separate jarosite precipitation concept, three methods of solution exchange were carried out:

1. At times at which the ferric concentration in solution was just below the solubility level at the corresponding pH (~ 2.2).

2. At the same times, but with 2 h of agitation after lowering the pH from 2.2 to 1.8 and stopping aeration to facilitate reduction and redissolution of any jarosite formed before exchange.

3. Conducting the bioleach experiments at a lower pH (1.8).

The results of tests employing the three conditions above are shown in Tables 21-23. Since the Gibraltar concentrate contains negligible amounts of pyrrhotite and chalcocite, and since pyrite is not leached, it is assumed that all copper and iron leached come from chalcopyrite. Thus iron deportments were calculated on a copper basis.

To calculate the acid requirements, the following formulae were used:

$$CuFeS_2 + O_2 + 2H_2SO_4 \rightarrow CuSO_4 + FeSO_4 + 2S^\circ + 2H_2O \quad (19)$$

Thus, one mole H_2SO_4 is used both for copper and iron.

Then the ferrous iron is oxidized, and ferric iron precipitates (to jarosite):

$$6FeSO_4 + 3H_2SO_4 + 3/2O_2 \rightarrow 3Fe_2(SO_4)_3 + 3H_2O \quad (20)$$

$$3Fe_2(SO_4)_3 + 12H_2O \rightarrow 2HFe_3(OH)_6(SO_4)_2 + 2H_2SO_4 \quad (21)$$

Adding reactions (20) and (21):

$$6FeSO_4 + 3/2O_2 + 9H_2O \rightarrow 2HFe_3(OH)_6(SO_4)_2 + 2H_2SO_4 \quad (22)$$

Thus, for the net reaction, 6 mol iron oxidized and hydrolyzed return 2 mol acid due to jarosite formation. The total acid requirement can therefore be given as:

Acid requirement = [Cu] extracted + [Fe] extracted
+ ([Fe] precipitated - [Fe/3] acid returned).

The results show that the bulk of jarosite formation in the leach tank can be avoided by solution exchange. This may be facilitated by temporarily lowering the pH prior to exchange or by running the leach at a lower pH. In this way, 80% of the jarosite formation can be handled separately. Although the results in Table 22 indicate almost complete jarosite avoidance in the leach tank, it should be noted that the leach was terminated at a lower copper extraction value. If the leach had been run longer, it could be expected that a higher oxidation potential would have been obtained, and some in-situ jarosite formation started. In all cases, the actual quantities of sulphuric acid added exceeded the calculated acid requirements. This excess acid was required to maintain the solution at the operating pH, and for the solubilization of minor impurities.

Two possible flowsheet schemes incorporating the solution exchange concept are shown in Figure 17. Preliminary investigations of Scheme 1 have given a 90% silver recovery by thiosulphate leaching of the bioleach residue. A further 8% of the silver has been subsequently recovered by flotation for recycle with the unreacted chalcopyrite. Losses to the flotation tails were therefore 2%.

CONCLUSIONS

The results of this study to investigate the chemistry and biology involved in a biological leaching process, in which silver is added during the leaching of chalcopyrite, have shown that at oxidation potentials below 680 mV(SHE) the leach produces elemental sulphur and not sulphate as the sulphide oxidation product. This reaction is ensured through the addition of silver, thiosulphate and copper sulphate at the start of the leach to chemically activate the mineral prior to biological oxidation.

The experimental evidence obtained strongly suggests that the chemical activiation mechanism involves the formation of a silver-copper sulphide precipitate on the surface of the chalcopyrite mineral and which acts as a mixture or as a compound as the active participant in the chalcopyrite decomposition reactions. It is postulated that biological oxidation of the cupric sulphide precipitate is accompanied by the silver-catalyzed conversion of chalcopyrite to more cupric sulphide to re-establish the equilibrium in the surface layer.

The biological mechanisms involved in the process are not understood. It is clear that the presence of active bacteria is essential, but under the conditions of the leach, biochemical oxidation of sulphide to sulphate does not occur. It is postulated that either sulphide is no longer incorporated into the cell membrane so that elemental sulphur is formed at the mineral surface, or that an enzyme-mediated reaction within the cell membrane is inhibited so that the usual polymeric sulphur to sulphate conversion does not occur.

The uncertainty of the biological mechanisms involved has not prevented considerable progress being made in developing the catalyzed leach into a practical process. The chemical activation principle has been made to work on a continuous basis, allowing an overall

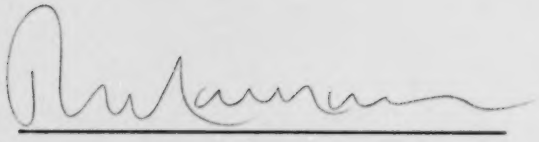
continuous activation-biological leach to be carried out. High copper extractions and stoichiometric sulphide conversion to elemental sulphur were achieved. Batch leach tests performed on a number of different concentrates indicate that the process is applicable to the treatment of chalcopyrite, bornite and other copper-containing concentrates. The selective leaching of chalcopyrite over pyrite has been demonstrated, and selectivity over other minerals is strongly indicated.

An important process requirement is the ability to recover and recycle the added silver catalyst. The formation of jarosite in the leach product has been shown to hinder recovery. A procedure is being developed which allows the separate formation of a silver-free jarosite outside of the leach tank. Recovery and recycle of the silver from the leach residue is therefore possible either with the unreacted chalcopyrite obtained in a flotation product and/or following a thiosulphate leach. Silver recoveries of 98% have been achieved.

Future work on process development should be carried out to further refine the silver recovery and recycle procedures. The ability of the procedures to effectively recover the precious metals originally contained in the concentrates needs to be established. Integrated continuous leach tests, including recycle of solid and solution streams, are required to demonstrate the silver recovery and recycle concepts for a number of different sulphide concentrates, and for different applications.

Although some preliminary investigations to substitute silver as catalyst have not shown any promising leads, further substitution studies are suggested. The substitution of silver by a lower cost catalyst may make the process more attractive to any prospective user.

An experimental investigation to define the bio-engineering aspects of the silver-catalyzed bioleach of chalcopyrite is to be undertaken. It is suggested that a substantial investigation could be carried out to determine the biochemical mechanisms of the involvement of T. ferrooxidans in the process.



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APPENDIX I

COPPER AND SULPHUR THROUGHPUT AND BALANCES FOR CONTINUOUS RUN

COPPER AND SULPHUR THROUGHPUT AND BALANCE FOR CONTINUOUS RUN

From the analytical and material balance data shown in Tables 8-11, the following calculations have been performed to determine the throughput and balances for copper and sulphur in the continuous leach run.

Assuming that no leaching takes place in the feed tank and conditioner, and by taking into account the unreacted chalcopyrite remaining in Tank 1 and Tank 2 at termination, we can subtract these unreacted components from the total input amounts to obtain the actual throughput as follows (referring to Table 11):

Copper Balance

Copper in concentrate	1209.6 g
Copper added as $CuSO_4 5H_2O$	436.3 g
TOTAL COPPER INPUT:	1209.6 g + 436.3 g = 1654.9 g

Subtracting the copper remaining in feed tank and conditioner (unreacted input)

Feed tank and conditioner (solution)	28.3 g
Feed tank and conditioner (solid)	69.7 g
TOTAL COPPER CARRIED:	1139.9 g + 408.0 g = 1547.9 g

Subtracting the copper found in Tank 1 and Tank 2 at termination (partially processed):

Tank 1			
Copper found in residue (70.2% unreacted $CuFeS_2$*)	91.3 g		
Copper leached (29.8% reacted $CuFeS_2$*)	38.7 g		
Copper found in solution from $CuSO_4 5H_2O$ (92.6-38.7)		53.9 g	
Subtotal	130.0 g	+ 53.9 g	= 183.9 g
Tank 2			
Copper found in residue (22.8% unreacted $CuFeS_2$*)	23.9 g		
Copper leached (77.2% reacted $CuFeS_2$*)	80.9 g		
Copper found in solution from $CuSO_4 5H_2O$ (135.4-80.9)		54.5 g	
Subtotal	104.8 g	+ 54.5 g	= 159.3 g
Total (Tank 1 + Tank 2)	234.8 g	+ 108.4 g	= 343.2 g
TOTAL COPPER CARRIED:	905.1 g	+ 299.6 g	= 1204.7 g

* Based on Tank 1 and Tank 2 residue copper assays of 17.7% and 5.75% respectively.

Continuous Process Products:

Solution	780.1 g + 299.6 g = 1079.7 g
Residue	148.3 g 148.3 g
TOTAL	928.4 g + 299.6 g = 1228.0 g

Cu extraction = 780.1/928.4 = 84%

Sulphur Balance (related to chalcopyritic sulphur)

Total sulphide sulphur input			1473.6 g
Calculated chalcopyritic sulphide/input			1217.8 g

Subtracting the unreacted chalcopyritic sulphide content of feed tank and conditioner

Feed tank (65.9 g Cu equivalent)			66.4 g
Conditioner (3.8 g Cu equivalent)			3.8 g
TOTAL CARRIED			1147.6 g

Subtracting the partially reacted chalcopyritic sulphide in Tank 1 and Tank 2 at termination

Tank 1 (unreacted	91.3 g Cu equiv.)	92.0 g	
(reacted	38.7 g Cu equiv.)	39.0 g	
Total	(130.0 g Cu)	131.0 g	131.0 g
Tank 2 (unreacted	23.9 g Cu equiv.)	24.1 g	
(reacted	80.9 g Cu equiv.)	81.5 g	
Total	(104.8 g Cu)	105.6 g	105.6 g
TOTAL CARRIED			911.0 g

Elemental sulphur found in:		
Tank 1 70.6 g		
Excess over reacted (39.0)	31.6 g	
Tank 2 115.3 g		
Excess over reacted (81.5)	33.8 g	
Total excess elemental sulphur*	65.4 g	
TOTAL CARRIED	65.4 g	911.0 g
Continuous Process Products:		
Residue (unreacted 198.3 g Cu equiv.)		149.4 g**
Elemental Sulphur	671.0 g	
OVERALL TOTALS (elemental sulphur produced and chalcopyritic sulphide decomposed)	736.4 g	761.6 g**
Chalcopyritic sulphide converted to S°	$\frac{736.4}{911.0}$	80.8%
Chalcopyritic sulphide reacted to produce S°	$\frac{736.4}{761.6}$	96.7%**
Total sulphuric acid used (S)		780 g
Elemental sulphur produced		185.9 g 671.0 856.9 g

* The transfer from Tank 1 to Tank 2 was at a 2/3 level of volume and from Tank 2 to settler from just above the bottom which could account for the "high floating" excess elemental sulphur.

** If adjustment is made that the final residue contained Cu also in the hydrolysed product (jarosite) see page 48; then 149.4 g should read 125.3g; 761.6 g should read 785.7; and 96.7% should be $\frac{736.4}{785.7}$ = 93.7% respectively.

APPENDIX II

CALCULATION OF THE POSSIBLE COMPOSITION OF THE CONTINUOUS LEACH SOLID PRODUCT

CALCULATION OF THE POSSIBLE COMPOSITION OF THE CONTINUOUS LEACH SOLID PRODUCT

The analytical and material balance data for the settler product composites shown in Tables 12 and 13 have been used to calculate the possible composition of the continuous leach solid product as follows:

Copper

Part of the copper value remaining in the residue has been found to be acid soluble and therefore in an oxidized form, probably as copper jarosite.

Total copper found	148.3 g	(or 16.0%)
copper acid soluble (in oxidized form)	24.0 g	(2.6%)
copper remaining unattacked (in sulphide form)	124.3 g	(13.4%)

Sulphide Balance

Sulphide was not determined. The values were calculated on the basis of the difference of $S_{total} - (S_{sulphate} + S_{elemental})$; and could be susceptible to errors.

The calculated sulphide values could be assigned as follows:

Total sulphide sulphur ($S^{=}$) found	324.4 g (S)
$CuFeS_2$ (124.3 g Cu corresponds to:)	125.3 g
Remaining sulphide	199.1 g

which, excluding other sulphides, should be as FeS_2.

Iron Balance

The iron balance is calculated from unoxidized sulphidic iron values and oxidized acid soluble iron numbers.

$CuFeS_2$ (124.3 g Cu corresponds to:)	109.2 g (Fe)
FeS_2 (199.1 g sulphide corresponds to:)	173.7 g

Total Iron in Sulphidic (unoxidized) Form

and assigned as $CuFeS_2$ + FeS_2	238.0 g
Fe in jarosite* (corresponding to 137.2 g $S(SO_4)$)	359.2 g
Total Fe sulphidic and hydrolysed basic sulphate	642.2 g
Total Fe found	668.2 g
Fe excess (not in sulphidic or acid soluble form)	26.2 g

* Calculated on the basic formula of $H_2Fe_6(OH)_{12}(SO_4)_4$ and the Cu (or Ag) substituting hydrogen and not iron.

From the above considerations and balances, we can assign a probable composition to the final products as follows.

Component	Weight (g)*	(%)	(%)**
Insoluble		10.5%	8.8%
Fe (excess)	26.2	0.9	0.8
FeS_2 (from $S^=$ 199.1 g)	372.8	12.3	10.4
$CuFeS_2$ (from Cu 124.3 g)	358.8	24.4	20.6
Cu (in acid soluble form)	24.0	0.8	0.7
Fe (in acid soluble form calculated as jarosite from $^{S}SO_4$ 137.2)	991.6+	32.8	27.8
S°	736.4	24.4	20.6
Ag (as oxide or sulphide)	3.5	0.1	0.1
Total		93.7	79.3
Wt. Loss		0	11.8
Not analysed constitutent		(6.3)	(8.9)
(Total)		(100)	(100)

* All total g found relate to the total final weight (3021.6 g)

** Recalculated on basis of 11.8% weight loss

\+ Calculated transfer loss (Tank 1 and Tank 2)

TABLE 1

HEAD ASSAYS OF CONCENTRATES

CONCENTRATE	ASSAY (%)							
	Cu	Fe	S	Zn	Sb	As	Ag	Insol.
Newmont	27.8	28.0	31.1					
Gibraltar	24.9	26.6	31.5					8.8
Whitehorse*	46.7	11.1	19.5				0.036	10.4
Equity	6.26	29.1	35.3		0.65	0.35	0.137	10.5
Selbaie*	27.9	25.3	31.9	9.7			0.027	3.5
Sumitomo C*	37.6	23.0	24.6		0.34	0.22		8.7
Sumitomo P*	14.8	32.3	44.9			3.66		
Magma	28.4	30.3	31.5			0.05		7.0

* Assay provided by sponsor.

TABLE 2

PROBABLE MINERALOGICAL COMPOSITION OF CONCENTRATES

CONCENTRATE	MINERALOGICAL COMPOSITION
Newmont	Chalcopyrite, pyrite
Gibraltar	Chalcopyrite, pyrite
Whitehorse	Bornite, minor vallerite, covellite, chalcocite, cuprite
Equity	Pyrite, chalcopyrite, minor tetrahedrite, tennantite, arsenopyrite
Selbaie	Chalcopyrite, sphalerite
Sumitomo C	Chalcopyrite, enargite, tetrahedrite, tennantite, pyrite
Sumitomo P	Pyrite, enargite, djurleite
Magma	Chalcopyrite

TABLE 3

SCREEN ANALYSIS OF CONCENTRATES

SCREEN SIZE (TYLER)	PERCENT BY WEIGHT RETAINED					
	GIBRALTAR AS-RECEIVED	GIBRALTAR BALLMILLED	WHITEHORSE AS-RECEIVED	WHITEHORSE BALLMILLED	EQUITY AS-RECEIVED	SELBAIE AS-RECEIVED
+35 mesh			1.3			0
+48			3.9		0	0.4
+65			3.0		0.1	1.5
+100			4.2		0.4	3.0
+150			6.9		1.8	5.5
+200			11.6		4.7	10.9
+325	48.7	2.8	15.8	0	12.9	
+400	6.5	3.7	16.7	0.6	9.9	29.6
-400	44.8	93.5	36.6	99.4	70.2	49.1
	100.0	100.0	100.0	100.0	100.0	100.0

SCREEN SIZE (TYLER)	PERCENT WEIGHT RETAINED			SCREEN SIZE (TYLER)	PERCENT WEIGHT RETAINED	
	NEWMONT BALLMILLED	MAGMA AS-RECEIVED	MAGMA BALLMILLED		SUMITOMO C AS-RECEIVED	SUMITOMO C BALLMILLED
+35 mesh		0.2		+35 mesh	0.6	0.1
+48		0.2		+48	0.6	0.1
+65		0.4	0	+65	0.7	0.1
+100		1.5	0.2	+100	1.8	0.3
+150		3.1	0.3	+150	4.6	0.4
+200		6.1	0.4	+200	10.3	1.2
+325	5.5	15.4	0.3	+325	20.6	2.1
+400	2.7	11.1	0.2	-325	60.8	95.7
-400	91.8	62.0	98.6			
	100.0	100.0	100.0		100.0	100.0

TABLE 4

CATALYZED BIOLEACH OF NEWMONT CONCENTRATE

Leach Conditions: Standard
Head Assay: 27.8% Cu, 28.0% Fe, 31.0% S_T, 5.5% insol
Residue Assay: 4.9% Cu, 19.4% Fe, 40.0% S_T, 26.8% S°, 7.1% insol
Solution Assay: 51.9 g/L Cu, 13.7 g/L Fe

INPUT	Cu	Fe	$S^=$	S°	S_{SO_4}	S_T	Insol
1.8 L 9K					2.5	2.5	
142.8 g $CuSO_4.5H_2O$	36.3				18.3	18.3	
1.16 g Ag_2SO_4					0.2	0.2	
12.4 g $Na_2S_2O_3.5H_2O$				1.6	1.6	3.2	
400 g Concentrate	111.2	112.0	122.0		2.0	124.0	22.0
75 g Inoculum:							
leached	1.2	0.9				1.2	
unattacked	3.0	3.3	3.5		1.2	3.5	0.8
426 mL H_2SO_4					81.8	81.8	
Total (g)	151.7	116.2	125.5	1.6	107.6	234.7	22.8
Products							
Solution: 2170 mL	112.6	29.7			80.4	80.4	
Wash Solution: 1270 mL	20.4	5.6			15.1	15.1	
Residue: 345.7 g	16.9	67.1	N.A.	92.7	N.A.	139.0	24.4
Total (g)	149.9	102.4	-	92.7	-	234.6	24.4
Cu Extraction:	(114.2-16.9)		= 97.3 g		1.53 M	(= 85.2%)	
S° Produced:	(92.7-1.6)		= 91.1 g		2.85 M		
$S(H_2SO_4)$ Consumed:			81.8 g		2.55 M		
Mole Ratios:			S°/Cu:		1.86		
			$S(H_2SO_4)/S°$:		0.89		
			$S(H_2SO_4)/Cu$:		1.67		

TABLE 5

CATALYZED BIOLEACH OF GIBRALTAR CONCENTRATE

Leach Conditions: Standard; as-received concentrate
Head Assay: 24.9% Cu, 26.6% Fe, 31.5% S_T, 8.8% insol
Residue Assay: 3.2% Cu, 19.9% Fe, 39.6% S_T, 26.9% S°, 9.0% insol
Solution Assay: 48.5 g/L Cu, 10.9 g/L Fe

INPUT	Cu	Fe	$S^=$	S°	S_{SO_4}	S_T	Insol
1.8 L 9K					2.5	2.5	
142.8 g $CuSO_4.5H_2O$	36.3				18.3	18.3	
1.16 g Ag_2SO_4					0.2	0.2	
12.4 g $Na_2S_2O_3.5H_2O$				1.6	1.6	3.2	
400 g Concentrate	99.6	106.4	122.8		3.2	126.0	35.2
75 g Inoculum:							
leached	1.2	0.9			1.2	1.2	
unattacked	3.0	3.3	3.5			3.5	0.8
399 mL H_2SO_4					76.6	76.6	
Total (g)	140.1	110.6	126.3	1.6	103.8	231.5	36.0
Products							
Solution: 2390 mL	115.9	26.1			81.5	81.5	
Wash Solution: 1195 mL	15.6	4.3			12.1	12.1	
Residue: 365.6 g	11.7	72.8	28.4	98.4	17.8	144.6	32.8
Total (g)	143.2	103.2	28.4	98.4	111.4	238.2	32.8

Cu Extraction:	(102.6-11.7) = 91.2 g	1.44 M	(= 88.6%)
S° Produced:	(98.4-1.6) = 96.8 g	3.03 M	
$S(H_2SO_4)$ Consumed:	76.6 g	2.39 M	
Mole Ratios:	S°/Cu:	2.11	
	$S(H_2SO_4)/S°$:	0.79	
	$S(H_2SO_4)/Cu$:	1.66	

TABLE 6

CATALYZED BIOLEACH OF GIBRALTAR CONCENTRATE

Leach Conditions: Standard; reground concentrate
Head Assay: 24.9% Cu, 26.6% Fe, 31.5% S_T, 8.8% insol
Residue Assay: 1.8% Cu, 21.9% Fe, 36.0% S_T, 25.6% S°, 7.7% insol
Solution Assay: 53.8 g/L Cu, 11.4 g/L Fe

INPUT	Cu	Fe	$S^=$	S°	S_{SO_4}	S_T	Insol
1.8 L 9K					2.5	2.5	
142.8 g $CuSO_4.5H_2O$	36.3				18.3	18.3	
1.16 g Ag_2SO_4					0.2	0.2	
12.4 g $Na_2S_2O_3.5H_2O$				1.6	1.6	3.2	
400 g Concentrate	99.6	106.4	122.8		3.2	126.0	35.2
75 g Inoculum:							
leached	1.2	0.9			1.2	1.2	
unattacked	3.0	3.3	3.5			3.5	0.8
400 mL H_2SO_4					76.8	76.8	
Total (g)	140.1	110.6	126.3	1.6	103.8	231.7	36.0
Products							
Solution: 1980 mL	106.5	22.6			75.0	75.0	
Wash Solution: 1280 mL	27.2	6.5			19.5	19.5	
Residue: 383.6 g	6.8	84.2	19.3	98.0	20.6	137.9	29.7
Total (g)	140.5	113.3	19.3	98.0	115.1	232.4	29.7
Cu Extraction:	(102.6-6.8)		= 95.8 g		1.51 M	(= 93.4%)	
S° Produced:	(98.0-1.6)		= 96.4 g		3.01 M		
$S(H_2SO_4)$ Consumed:			76.8 g		2.40 M		
Mole Ratios:			S°/Cu:		2.00		
			$S(H_2SO_4)/S°$:		0.80		
			$S(H_2SO_4)/Cu$:		1.59		

TABLE 7

CONTINUOUS SILVER CATALYZED BIOLEACH
OF GIBRALTAR CONCENTRATE

(Cumulative Data)

LEACH TIME (h)	Cu IN FEED (as $CuFeS_2$) (g)	H_2SO_4 ADDED (12N EQUIV) mL	Cu IN SOLUTION g	Cu ADDED as $CuSO_4$ g	Cu LEACHED g	Cu EXTRACTION %	Cu LEACH RATE* mg/L/h
0	100.8	0	34.13	36.96	0	0	-
25	100.8	1	34.61	36.96	0	0	0
70	100.8	11	40.20	36.96	3.24	3.2	38
90	100.8	36	52.35	36.96	15.3	15.3	301
114	100.8	86	76.87	36.96	39.91	39.6	444
122	100.8	146	83.92	36.96	46.96	46.6	427
Start of Continuous Feed							
138	126.0	269	118.83	46.04	72.79	54.4	614
144	144.9	314	131.65	52.85	78.80	54.4	358
162	170.1	404	168.04	61.94	106.10	62.4	402
186	217.5	567	214.65	79.04	135.61	62.4	370
213	243.5	664	246.35	88.40	157.95	64.9	324
238	260.3	776	287.16	94.46	192.71	74.0	324
258	275.6	841	291.44	99.63	191.48	69.5	270
282	284.5	888	308.93	103.16	205.77	72.5	227
306	300.4	936	333.64	108.88	224.76	74.8	196
330	338.3	1003	359.92	122.54	237.38	70.2	178
354	363.9	1070	390.88	131.78	259.10	71.2	149
379	394.7	1170	400.82	142.86	257.96	65.4	138
407	425.4	1279	431.06	153.95	277.11	65.1	142
426	447.6	1356	445.57	161.96	283.61	63.4	127
450	461.5	1480	501.62	165.10	336.52	72.9	200
475	487.6	1581	536.41	174.52	361.87	74.2	214
498	511.3	1656	555.80	183.04	372.76	72.9	243
523	531.2	1709	584.13	190.22	393.91	74.2	256
548	559.2	1784	611.75	200.31	411.44	73.6	263
573	584.1	1863	639.99	209.29	430.70	73.7	195
596	618.3	1966	659.38	221.63	437.75	70.8	160
619	660.3	2101	708.62	236.79	471.85	71.5	202
643	691.4	2254	755.22	247.98	507.24	73.4	240
667	734.9	2423	808.35	263.69	544.66	74.1	276
690	782.8	2603	865.97	280.96	585.01	74.7	327
717	826.4	2785	924.99	296.66	628.33	76.0	374
740	876.2	2966	974.80	314.61	660.19	75.4	359
763	930.9	3171	1040.58	334.35	706.23	75.9	369
787	995.7	3401	1141.81	357.69	757.13	76.0	387
811	1035.5	3591	1149.75	372.04	777.72	75.1	356
835	1091.5	3819	1221.21	392.22	829.99	76.0	388
859	1155.6	4065	-	415.33	-	-	-

* Leach Rate calculated as a 5 day moving average during continuous leaching.

TABLE 8

CONTINUOUS BIOLEACH: SETTLER ANALYTICAL DATA

TIME (h)	SOLUTION (g/L)		RESIDUE (%)					
	Cu	Fe	SETTLER LAYER*	Cu	Ag	Fe	S°	INSOL
186	34.410	6.065	T	4.40	0.196	25.45	18.5	9.3
213	36.780	6.880	T	2.25	0.178	25.80	13.4	10.1
239	37.195	6.990	T	3.80	0.162	23.95	21.4	9.8
306	40.105	8.100	T	3.95	0.158	22.85	21.2	9.7
354	36.040	6.960	T	5.15	0.149	22.85	20.9	9.3
407	34.750	6.885	T	4.90	0.14	22.85	20.9	9.6
450	35.130	8.030	T	2.99	0.15	23.86	16.1	12.5
475	37.490	9.390	T	2.58	0.14	22.87	18.0	11.5
523	36.275	8.385	T	3.10	0.14	21.88	18.9	12.0
574	36.705	8.465	T	3.58	0.14	22.87	17.2	11.0
596	31.960	7.855	T	2.50	0.12	25.4	10.3	13.6
			B	7.30	0.10	21.5	25.5	8.8
619	29.470	7.705	T	2.60	0.12	25.4	11.1	13.3
			B	7.35	0.10	21.2	27.2	8.3
643	30.210	8.370	T	2.30	0.11	25.4	9.7	13.5
			B	6.85	0.10	22.4	26.0	9.0
667	29.850	8.140	T	2.50	0.10	25.4	10.3	13.8
			B	7.0	0.10	22.0	25.9	8.9
690	27.205	7.480	T	2.9	0.10	21.4	17.9	13.7
			B	7.44	0.10	22.05	27.6	8.6
717	30.450	8.160	T	4.30	0.10	19.9	23.5	11.4
			B	5.15	0.10	22.05	24.0	10.8
740	35.945	9.160	NS	4.85	0.10	21.75	23.0	10.6
763	38.090	9.500	NS	4.20	0.08	20.75	22.7	12.8
770	36.390	9.165	NS	5.15	0.10	20.75	24.4	10.0
787	34.020	9.745	NS	5.25	0.10	20.35	24.9	11.3
811	30.905	8.495	NS	5.00	0.11	19.50	27.9	10.7
835	28.350	8.455	NS	4.75	0.10	20.75	25.0	11.5

* SETTLER LAYER - T = top layer
B = bottom layer
NS = no separation of layers

TABLE 9

CONTINUOUS BIOLEACH: SETTLER MATERIAL BALANCE

TIME (h)	ORIGINAL VOL (mL)	SOLUTION & WASH			RESIDUE						
		VOL (mL)	Cu (g)	Fe (g)	QUANTITY (g)	SETTLER LAYER*	Cu (g)	Ag (g)	Fe (g)	S° (g)	INSOL (g)
186	840	1100	37.8	6.67	62.2	T	2.73	0.122	15.83	11.5	5.80
213	840	1060	39.0	7.29	45.0	T	1.01	0.080	11.61	6.0	4.54
239	839	1300	48.4	9.07	151.4	T	5.75	0.246	36.26	32.4	14.84
306	818	1200	48.2	9.72	162.5	T	6.42	0.256	37.13	34.5	15.76
354	819	1220	43.9	8.49	170.9	T	8.80	0.254	39.05	35.7	15.89
407	828	1315	45.7	9.05	162.2	T	7.95	0.227	37.06	33.9	15.57
450	850	1240	43.6	9.96	68.9	T	2.06	0.103	16.44	11.1	8.61
475	860	1180	44.3	11.08	67.3	T	1.74	0.094	15.39	12.1	7.74
523	850	1270	46.1	10.65	72.8	T	2.26	0.102	15.93	13.7	8.75
574	845	1225	45.1	10.37	75.1	T	2.67	0.105	17.18	12.9	8.28
596	849	1610	51.5	12.65	36.5	T	0.91	0.043	9.27	3.8	4.96
					161.3	B	11.78	0.161	34.68	41.1	14.19
619	867	1785	52.6	13.75	48.1	T	1.25	0.057	12.21	5.3	6.40
					142.7	B	10.49	0.143	30.25	38.8	11.84
643	861	1680	50.7	14.06	41.1	T	0.94	0.045	10.44	4.0	5.55
					138.6	B	9.50	0.139	31.05	36.0	12.47
667	876	1650	49.3	13.43	40.8	T	1.02	0.040	10.36	4.2	5.63
					124.2	B	8.69	0.124	27.32	32.2	11.05
690	911	1820	49.5	13.61	66.2	T	1.92	0.066	14.17	11.8	9.07
					89.0	B	6.62	0.089	19.62	24.6	7.65
717	990	1665	50.5	13.59	36.0	T	1.55	0.036	7.16	8.5	4.10
					109.7	B	5.65	0.110	24.19	26.3	11.85
740	948	1480	53.2	13.56	151.6	NS	7.35	0.152	32.97	34.9	16.07
763	861	1290	49.1	12.26	139.0	NS	5.84	0.110	28.84	31.6	17.79
770	882	1370	49.9	12.56	138.4	NS	7.13	0.138	28.72	33.8	13.84
787	1826	2640	89.8	25.73	274.0	NS	14.38	0.274	55.76	68.2	30.96
811	884	1500	46.3	12.74	126.0	NS	6.30	0.138	24.57	35.1	13.48
835	880	1600	45.2	13.53	120.1	NS	5.70	0.120	24.92	30.0	13.81
Subtotal T					1307		48.9	1.876	305.49	239.2	141.49
B					765.5		52.7	0.766	167.11	198.2	69.05
NS					949.1		46.7	0.933	195.78	233.6	105.95
TOTAL	20024	32200	1079.7	263.84	3021.6		148.3	3.575	668.38	671.0	316.49

* SETTLER LAYER - T = top layer
B = bottom layer
NS = no separation of layers

TABLE 10

CONDENSED ANALYTICAL DATA FOR CONTINUOUS RUN MATERIAL BALANCE

		Cu	Fe	$S_{SO_4^=}$ (g/L)	S°	S_T or	$S^=$ (%)	Ag	INSOL
GIBRALTER CONC.		25.2	28.0	.8		31.5	(30.7)	.00299	8.8
($CuFeS_2$ fraction)		25.2	22.1			25.4	(25.4)		
$CuSO_4 5H_2O$		25.5		12.8		12.8			
Ag_2SO_4				10.3				69.2	
Feed tank	(solution)	26.1	.13						
	(solid)	26.4	27.7	.8	NIL	31.4	(30.7)	-	8.7
Conditioner	(solution)	23.4	.48						
	(solid)	26.6	27.7	.8	NIL	31.8	(31.0)	0.13	8.3
Primary reactor	(solution)	40.3	10.8						
	(solid)	17.7	24.7	2.2	13.7	37.5	(21.6)	0.12	8.7
Secondary reactor	(solution)	48.3	17.4						
	(solid)	5.75	21.7	6.0	27.7	43.2	(9.5)	0.11	8.8
Leach solution (combined)		54.0	13.1	36.6	-	36.6	-	-	-
Residue (top layer)		3.75	23.4	5.8	18.3	31.2	(7.2)	0.144	10.8
(bottom layer)		6.88	21.8	3.3	25.9	42.3	(13.1)	0.100	9.0
(non/separated)		4.92	20.6	3.8	24.6	42.1	(13.7)	0.098	11.1
(combined)		4.91	22.1	4.5	22.2	37.4	(10.7)	0.118	10.4

( ) Calculated Values.

TABLE 11

MATERIAL BALANCE FOR CONTINUOUS RUN

	Quantity g or mL	Cu	Fe	$S_{SO_4^=}$	S°	S_T	$(S^=)$	Ag	INSOL
					g (total)				
INPUT									
Gibraltar Conc.	4800	1209.6	1344	38.4		1512	1473.6	.1374	422.4
($CuFeS_2$ fraction)	(3490)	(1209.6)	(1062.7)			(1217.8)	(1217.8)		
$CuSO_4 5H_2O$	1713	436.3		218.8		218.8			
Ag_2SO_4	5.7			0.4		0.4		4.400	
$Na_2S_2O_3 5H_2O$	121.8					31.4			
9K (nutrient) $(NH_4)_2SO_4$	64.8			15.7		15.7			
$MgSO_4 7H_2O$	11.2			1.4		1.4			
Subtotal		1645.9	1344	274.7		1779.7	1473.6	4.5374	422.4
$12NH_2SO_4$	4065			780.5		780.5			
TOTAL (1)		1645.9	1344	1055.2		2560.2	1473.6	4.5374	422.4
Remaining Unprocessed at Termination in									
Feed tank (solution)	1030	26.9	.1	13.6	-	13.6			
(solid)	249.5	65.9	69.1	(2.0)	NIL	78.3	(76.3)	NIL	21.7
Conditioner (solution)	60	1.4	.3	.9	-	.9			
(solid)	14.2	3.8	3.9	(.1)	NIL	4.5	(4.4)	.0018	1.2
Subtotal (a)		98.0	73.4	16.6	NIL	97.3	80.7	.0018	22.9
Partially Processed in									
Primary reactor (solution)	2300	92.6	24.9	60.9	-	60.9			
(solid)	515.6	91.3	127.3	11.4	70.6	193.3	(111.3)	.619	44.8
Secondary reactor (solution)	2800	135.4	48.6	95.8	-	95.8			
(solid)	416.1	23.9	90.2	24.9	115.3	179.7	(39.5)	.458	33.6
Subtotal (b)		343.2	291.0	193.0	185.9	529.7	(150.8)	1.077	78.4
TOTAL (2)		441.2	364.4	209.6	185.9	627.0	(231.5)	1.099	101.3
Throughput									
(Total 1 - Total 2)		1204.7	979.6	845.6	(65.4)	1998.6	1242.1	3.528	321.1
		1204.7	979.6	845.6	65.4	1998.6	1242.1	3.528	321.1
PRODUCTS									
Leach solution	20024	1079.7	263.8	732		732			
(transfer from primary and secondary reactor)	65.4				65.4	65.4			
Residue	3021.6	148.3	668.4	137.2	671	1132.5	(324.3)	3.575	316.5
TOTAL (3)		1228	932.2	869.2	736.4	1929.9	(324.3)	3.575	316.5

TABLE 12

ANALYTICAL DATA OF SETTLER COMPOSITES (%)

	Cu	Cu_{SOL}	Fe	Fe_{SOL}	$S_{SO_4^=}$	S°	S_T	$(S^=)$	Ag	INSOL
Top layer	3.75	1.02	23.4	16.2	5.8	18.3	31.2	(7.2)	0.144	10.8
Bottom layer	6.88	.82	21.8	9.8	3.3	25.9	42.3	(13.1)	0.100	9.0
No separation of layers	4.92	.46	20.6	6.6	3.8	24.6	42.1	(13.7)	0.098	11.1

TABLE 13

MATERIAL BALANCE OF SETTLER PRODUCTS

	QUANTITY	Cu	Cu_{SOL}	Fe	Fe_{SOL}	$S_{SO_4^=}$	S°	S_T	$(S^=)$	Ag	INSOL
	(g)					g/total					
Top layer	1307	49.01	13.33	305.8	211.7	75.8	239.2	407.8	94.1	1.882	141.2
Bottom layer	765.5	52.66	6.28	166.9	75.0	25.3	198.3	323.8	100.3	.765	68.9
No separation of layers	949.1	46.70	4.36	195.5	62.6	36.1	233.5	399.6	130.0	.930	105.4
Total (g)	3021.6	148.3	23.97	668.2	349.3	137.2	671.0	1131.2	324.4	3.577	315.5
Calculated (%)		4.91	.79	22.1	11.6	4.5	22.2	37.4	10.7	0.118	10.5

TABLE 14

CATALYZED BIOLEACH OF EQUITY CONCENTRATE

Leach Condition: standard
Head Assay: 6.26% Cu, 29.14% Fe, 14.9% insol, 0.137% Ag, 0.37% As, 0.65% Sb, 0.067% Bi
Residue Assay: 0.98% Cu, 26.8% Fe, 14.6% insol, 0.30% Ag, 0.34% As, 0.56% Sb, 0.063% Bi, 7.05% S°
Solution Assay: 27.16 g/L Cu, 2.22 g/L Fe 12N H_2SO_4 Consumed: 56 mL

INPUT	Cu	Fe	Ag	Insol	As	Sb	Bi	S°
400 g concentrate	25.0	116.6	0.55	59.6	1.48	2.60	0.27	
142.8 g $CuSO_4.5H_2O$	36.3							
75 mL inoculum	4.0							
1.16 g Ag_2SO_4			0.80					
Total (g)	65.3	116.6	1.35	59.6	1.48	2.60	0.27	
PRODUCTS								
2.24 L Solution	60.84	5.0						
0.62 L Wash	3.60	0.4						
397.7 g Residue	3.89	106.5	1.19	58.0	1.35	2.23	0.25	28.03
Total (g)	68.3	112.9	1.19	58.0	1.35	2.23	0.25	28.03

Cu Extraction	= (25.0-3.89) = 21.11 g	= 0.33 M (= 84.4%)	
S° Produced	= 28.03 g	= 0.87 M	
$S(H_2SO_4)$ Consumed	= 10.75 g	= 0.34 M	
Mol Ratios	S°/Cu	= 2.63	
	$S(H_2SO_4)/S^{\circ}$	= 0.39	
	$S(H_2SO_4)/Cu$	= 1.03	

TABLE 15

CATALYZED BIOLEACH OF EQUITY CONCENTRATE

Leach Condition: no silver
Head Assay: 6.26% Cu, 29.14% Fe, 35.3% S, 14.9 insol, 0.137% Ag
Residue Assay: 1.60% Cu, 29.8% Fe, 0.12% Ag, 14.2% insol, 5.50% S
Solution Assay (incl. wash): 20.78 g/L Cu, 2.11 g/L Fe
12N H_2SO_4 Consumed: 60 mL

INPUT	Cu	Fe	Ag	Insol	S°
400 g concentrate	25.0	116.6	0.55	59.6	
142.8 g $CuSO_4.5H_2O$	36.3				
75 mL inoculum	0.7				
0 g Ag_2SO_4					
Total (g)	62.0	116.6	0.55	59.6	
PRODUCTS					
2.68 L Solution	55.69	5.7			
378.1 g Residue	6.05	112.7	0.45	56.7	20.8
Total (g)	61.7	118.4	0.45	56.7	20.8

Cu Extraction	= (25.0-6.05) = 18.95 g	= 0.30 M	(= 75.8%)
S° Produced	= 20.80 g	= 0.65 M	
$S(H_2SO_4)$ Consumed	= 11.52 g	= 0.36 M	
Mol Ratios	$S°/Cu$	= 2.17	
	$S(H_2SO_4)/S°$	= 0.55	
	$S(H_2SO_4)/Cu$	= 1.20	

TABLE 16

CATALYZED BIOLEACH OF EQUITY CONCENTRATE

Leach Condition: 1/2 silver
Head Assay: 6.26% Cu, 29.14% Fe, 35.3% S, 14.9 insol, 0.137% Ag
Residue Assay: 2.04% Cu, 28.84% Fe, 0.24% Ag, 14.5% insol, 3.66% S
Solution Assay (incl. wash): 17.46 g/L Cu, 1.75 g/L Fe
12N H_2SO_4 Consumed: 47 mL

INPUT	Cu	Fe	Ag	Insol	S°
400 g concentrate	25.0	116.6	0.55	59.6	
142.8 g $CuSO_4.5H_2O$	36.3				
75 mL inoculum	0.7				
0.58 g Ag_2SO_4			0.40		
Total (g)	62.0	116.6	0.95	59.6	
PRODUCTS					
2.86 L Solution	49.93	5.0			
375.7 g Residue	7.66	108.3	0.90	54.3	13.75
Total (g)	57.59	113.3	0.90	54.3	13.75
Cu Extraction	= (25.0-7.66)	= 17.34 g		= 0.27 M (= 69.4%)	
S° Produced		= 13.75 g		= 0.43 M	
$S(H_2SO_4)$ Consumed		= 9.02 g		= 0.28 M	
Mol Ratios		S°/Cu		= 1.59	
		$S(H_2SO_4)/S°$		= 0.65	
		$S(H_2SO_4)/Cu$		= 1.04	

TABLE 17

CATALYZED BIOLEACH OF EQUITY CONCENTRATE

Leach Condition: standard
Head Assay: 6.26% Cu, 29.14% Fe, 35.3% S, 14.9 insol, 0.137% Ag
Residue Assay: 1.40% Cu, 26.6% Fe, 0.32% Ag, 14.3% insol, 6.72% S
Solution Assay (incl. wash): 17.87 g/L Cu, 4.08 g/L Fe
12N H_2SO_4 Consumed: 56 mL

INPUT	Cu	Fe	Ag	Insol	S°
400 g concentrate	25.0	116.6	0.55	59.6	
142.8 g $CuSO_4.5H_2O$	36.3				
75 mL inoculum	0.7				
1.16 g Ag_2SO_4			0.80		
Total (g)	62.0	116.6	1.35	59.6	
PRODUCTS					
3.17 L Solution	56.65	12.9			
370.5 g Residue	5.18	98.6	1.19	52.9	24.90
Total (g)	57.59	111.5	1.19	52.9	24.90

Cu Extraction	= (25.0-5.18)	= 19.82 g	= 0.31 M (= 79.3%)
S° Produced		= 24.90 g	= 0.78 M
$S(H_2SO_4)$ Consumed		= 10.75 g	= 0.34 M
Mol Ratios		S°/Cu	= 2.52
		$S(H_2SO_4)/S°$	= 0.44
		$S(H_2SO_4)/Cu$	= 1.10

TABLE 18

CATALYZED BIOLEACH OF SELBAIE CONCENTRATE

Leach Condition: standard
Head Assay: 27.9% Cu, 25.3% Fe, 9.7% Zn, 31.9% S, 0.027% Ag, 3.5% insol
Residue Assay: 2.6% Cu, 18.92% Fe, 2.28% Zn, 0.28% Ag, 3.5% insol, 30.14%S°
Solution Assay (incl. wash): 44.68 g/L Cu, 10.39 g/L Fe, 9.38 g/L Zn

INPUT	Cu	Fe	Zn	Ag	Insol	S°
400 g concentrate	111.6	101.2	38.8	0.11	14.0	
142.8 g $CuSO_4.5H_2O$	36.3					
75 mL inoculum	0.6					
1.16 g Ag_2SO_4				0.80		
Total (g)	148.5	101.2	38.8	0.91	14.0	
PRODUCTS						
2790 mL Solution	124.65	28.98	26.17			
600 mL Wash	5.35	1.37	1.07			
Total (g)	130.0	30.35	27.24			
322.4 g Residue	8.38	61.00	7.35	0.90	11.4	97.17
Total (g)	138.38	91.35	34.59	0.90	11.4	97.17

Cu Extraction	= (111.6-8.38)	= 103.22 g	= 1.63 M (= 92.5%)
Zn Extraction	= (38.8-7.35)	= 31.45 g	= 0.48 M (= 81.1%)
$S(H_2SO_4)$ Consumed		= 81.79 g	= 2.56 M
S° Produced		= 97.17 g	= 3.04 M
Mol Ratios		S°/Cu	= 1.87
		$S(H_2SO_4)/S°$	= 0.84
		$S(H_2SO_4)/Cu$	= 1.57

TABLE 19

CATALYZED BIOLEACHING OF SUMITOMO C CONCENTRATE

Head Assay: 37.6% Cu, 23.0% Fe, 24.6% S, 8.7% Insol.

LEACH CONDITIONS	RESIDUE WEIGHT (g)	ASSAY		Cu EXTRACTION (%)	H_2SO_4 CONSUMED (mL)	MOL RATIOS		
		Cu	S°			S°/Cu	H_2SO_4/S°	H_2SO_4/Cu
Standard; As-Received	320.3	6.32	23.52	86.5	563	1.15	1.43	1.65
Standard; Ballmilled	309.5	6.12	24.79	87.4	496	1.16	1.24	1.44
Pretreated; Standard, Ballmilled	381.6	2.49	24.25	93.7	608*	1.30	1.26	1.64
Half Silver; Ballmilled	311.9	4.71	24.53	90.2	504	1.12	1.26	1.42

* Includes 92 mL added in pretreatment.

TABLE 20

Flotation of Continuous Bioleach Residue Composite

Product	Weight (%)	Assay (% or g/tonne)				Distribution on (%)			
		Cu	Fe*	S°	Ag	Cu	Fe	S°	Ag
Concentrate	64.4	7.40	6.50	30.9	967	94.2	56.2	81.5	60.8
Tails	35.6	0.83	9.00	12.7	1131	5.8	43.8	18.5	39.2
Calculated Head	100.0	5.06	7.33	24.4	1025	100.0	100.0	100.0	100.0

*acid soluble iron

TABLE 21

CATALYZED BIOLEACH WITH SOLUTION EXCHANGE #1

Conditions: 2L solution, 400 g Gibraltar concentrate [25.2% Cu, 22.1% Fe ($CuFeS_2$)], Exchange at pH 2.2

EXCHANGE #	RETENTION TIME (h)	pH	mV	SOLUTION (g/L) Fe^{2+}	Fe^{3+}	Fe_T*	LEACHED (g) Fe	Cu
1	90	2.20	405	3.60	4.41	8.89	17.78	33.38
2	120	2.24	420	3.52	1.35	5.56	11.11	15.11
3	168	2.25	410	2.50	0.66	3.59	7.18	12.87
Final	310	2.13	415	2.50	1.72	4.93	9.87	21.31

EXCHANGE #	Fe REMOVED (%)	(M)	Cu EXTRACTED (%)	(M)	Fe pptd** (%)	(M)	Fe (%) REMOVED	pptd	ACID REQUIREMENTS (M)	12N H_2SO_4 CONSUMED (mL)	(M)
1	20.1	0.301	33.1	0.526	13.0	0.225	61	39	0.965	157	0.942
2	12.6	0.199	15.0	0.238	2.4	0.039					
(Cumulative)	32.7	0.500	48.1	0.764	15.4	0.246	68	32	1.428	253	1.518
3	8.1	0.128	12.8	0.203	4.7	0.075					
(Cumulative)	40.8	0.628	60.9	0.907	20.1	0.361	67	33	1.749	315	1.890
Final	11.8	0.176	21.1	0.336	9.9	0.160					
(Cumulative)	52.0	0.804	82.0	1.243	30.0	0.439	65	35	2.340	412	2.472

* Fe^{2+}/Fe^{3+} determined by differential colorimetry. Total Fe determined by AA.

** Fe precipitating in leach tank calculated by difference.

TABLE 22

CATALYZED BIOLEACH WITH SOLUTION EXCHANGE #2

Conditions: Leach charge as in Table 21
Exchange following pH adjustment to 1.8.

EXCHANGE #	RETENTION TIME (h)	pH		mV	SOLUTION (g/L) Fe^{2+}	Fe^{3+}	Fe_T	LEACHED (g) Fe	Cu
1	95	2.05	1.80	425	6.67	2.74	11.5	31.7	35.6
2	140	2.23	1.80	420	6.17	2.63	10.2	20.4	23.3
Final	188	2.24	1.80	412	2.53	1.00	4.0	7.9	10.2

EXCHANGE #	Fe REMOVED (%)	(M)	Cu EXTRACTED (%)	(M)	Fe pptd (%)	(M)	Fe (%) REMOVED	pptd	ACID REQUIREMENTS (M)	12N H_2SO_4 CONSUMED (mL)	(M)
1	35.9	0.57	35.3	0.56	nil		100	0	1.13	198	1.19
2	23.1	0.37	23.1	0.38	nil						
(Cumulative)	59.0	0.94	58.4	0.94	nil		100	0	1.98	330	1.98
Final	9.0	0.14	10.1	0.16	1.1	0.02					
(Cumulative)	68.0	1.08	68.5	1.10	1.1	0.02	98	2	2.19	405	2.43

TABLE 23

CATALYZED BIOLEACH WITH SOLUTION EXCHANGE #3

Conditions: Leach charge as in Table 21
Bioleach and exchange at pH 1.8

EXCHANGE #	RETENTION TIME (h)	pH	mV	SOLUTION (g/L) Fe^{2+}	Fe^{3+}	Fe_T*	LEACHED (g) Fe	Cu
1	92	1.84	397	5.57	3.24	10.89	21.78	31.99
2	176	1.53	411	5.41	2.29	8.93	17.86	21.13
3	224	1.66	415	3.22	1.51	5.49	10.79	12.40
Final	416	1.88	530	1.06	4.41	5.41	10.84	25.09

EXCHANGE #	Fe REMOVED (%)	(M)	Cu EXTRACTED (%)	(M)	Fe pptd** (%)	(M)	Fe (%) REMOVED	pptd	ACID REQUIREMENTS (M)	12N H_2SO_4 CONSUMED (mL)	(M)
1	24.6	0.390	31.7	0.504	7.1	0.114	77.6	22.4	0.970	152	0.912
2	20.2	0.320	21.0	0.323	0.8	0.013					
(Cumulative)	44.8	0.710	52.7	0.837	7.9	0.127	85.0	15.0	1.547	290	1.740
3	12.4	0.197	12.3	0.195	-0.1	-0.002					
(Cumulative)	57.2	0.907	65.0	1.032	7.8	0.125	88.0	12.0	2.022	370	2.220
Final	12.3	0.194	24.9	0.395	12.6	0.205					
(Cumulative)	69.5	1.101	89.9	1.427	20.4	0.326	77.3	22.7	2.745	496	2.976

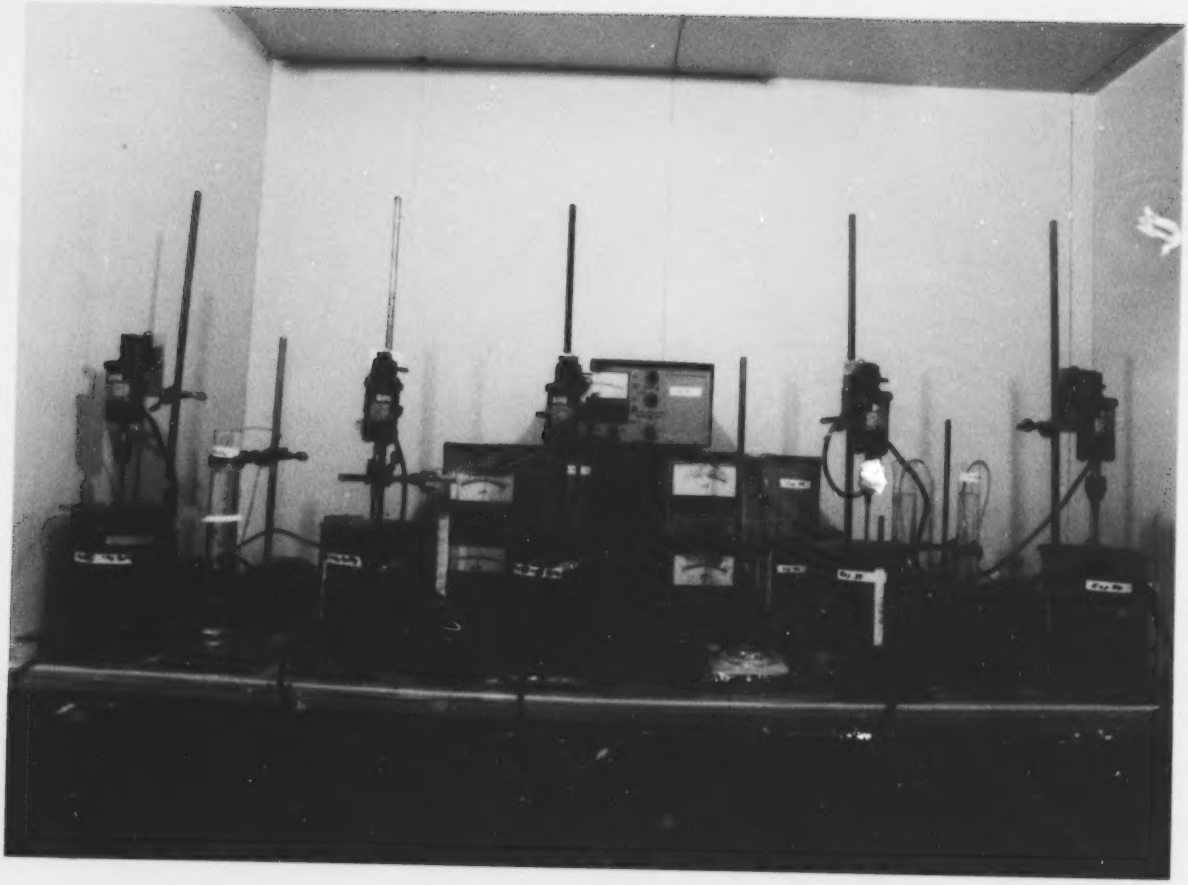
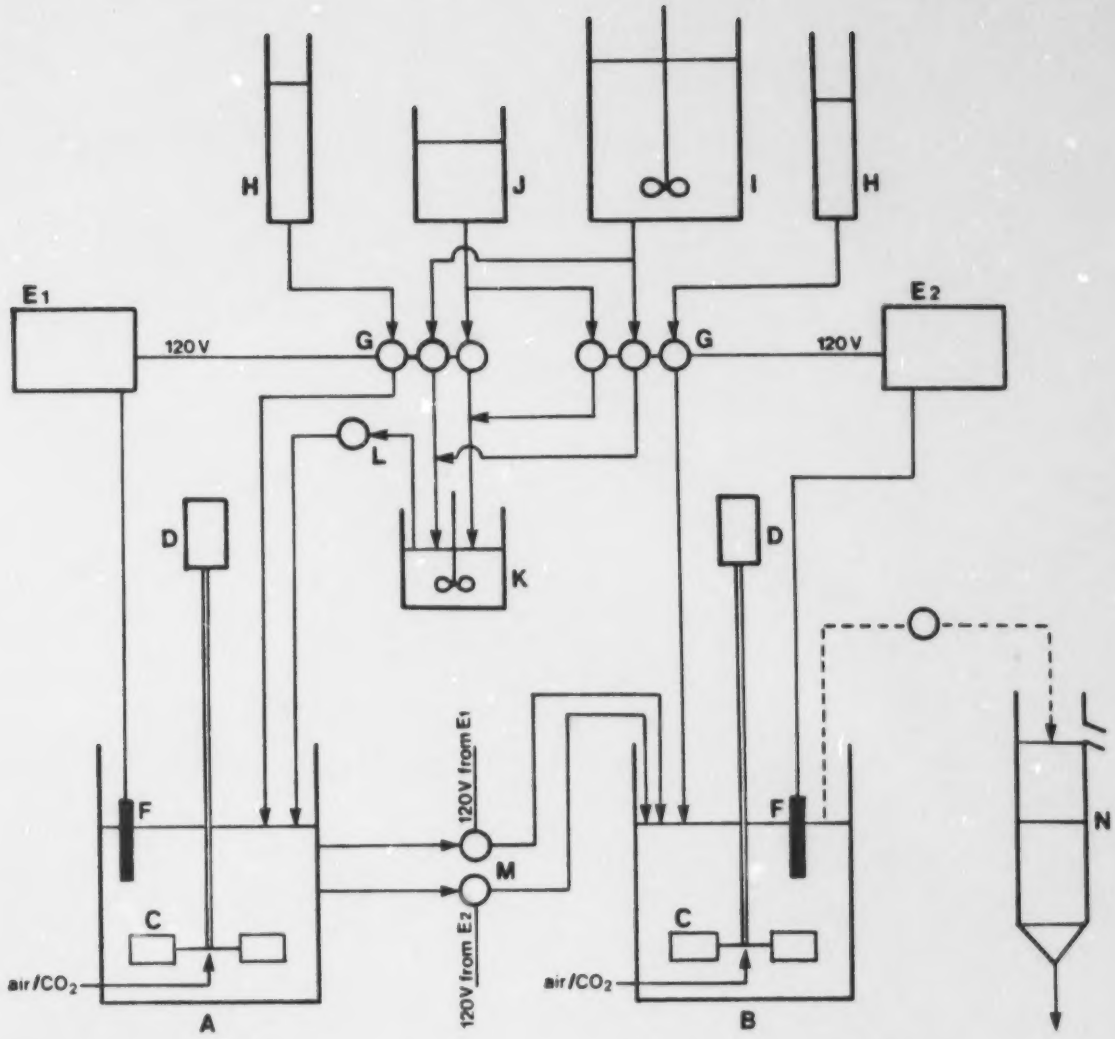


FIGURE 1

2 LITRE BIOLEACH TANKS AND CONTROL EQUIPMENT



A. LEACH TANK #1
B. LEACH TANK #2
C. TURBINE IMPELLER
D. STIRRER MOTOR
E_1, E_2. pH METER-CONTROLLER
F. pH ELECTRODE
G. 3-HEAD PUMP
H. SULPHURIC ACID RESERVOIRS
I. CONCENTRATE-$CuSO_4$ FEED
J. SILVER-THIOSULPHATE FEED
K. CONDITIONING TANK
L. FEED PUMP
M. LEACH TANK TRANSFER PUMPS
N. PRODUCT SETTLER

FIGURE 2

SCHEMATIC OF CONTINUOUS BIOLEACH EQUIPMENT

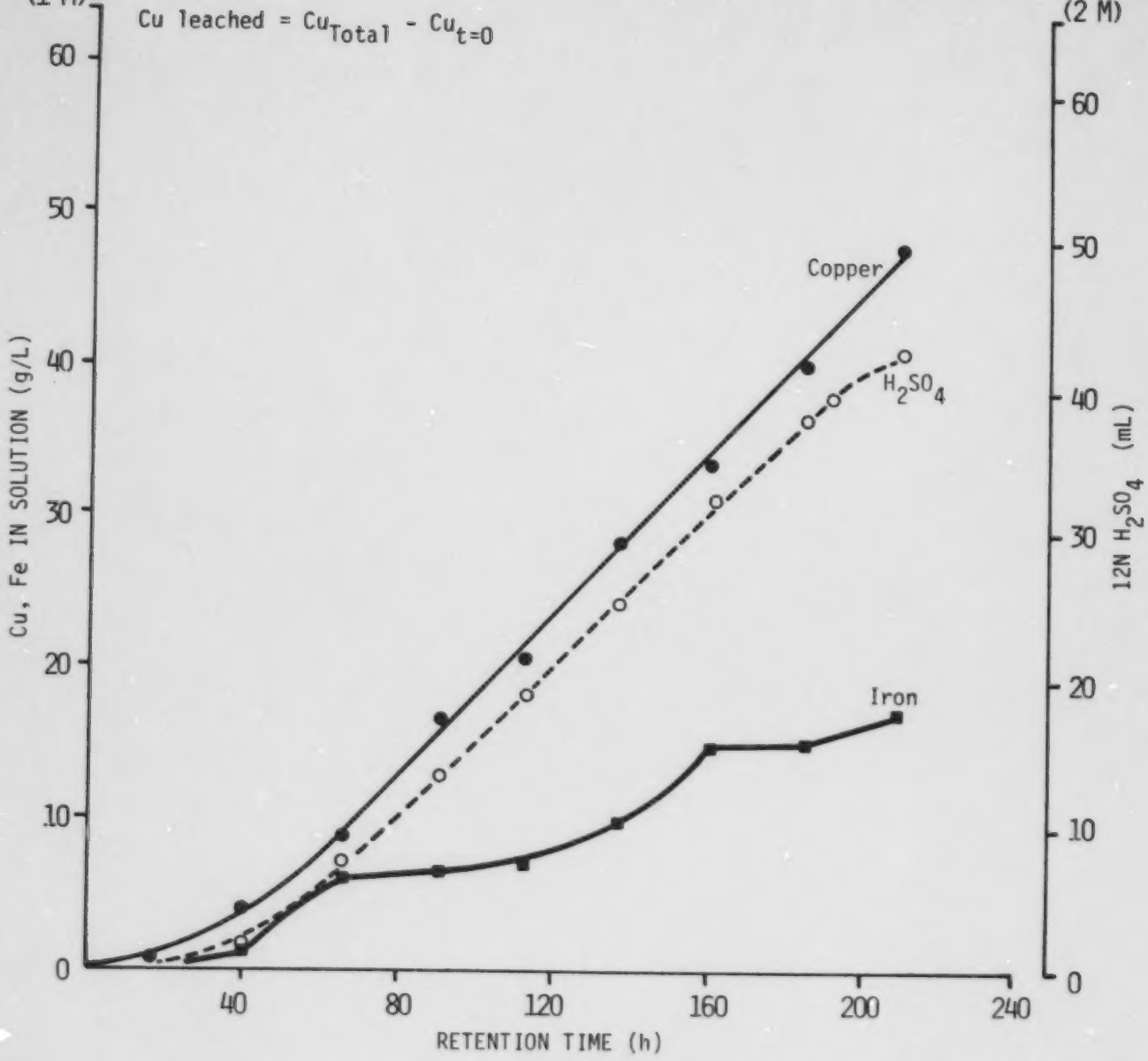


FIGURE 3

CATALYZED BIOLEACH OF NEWMONT CONCENTRATE UNDER STANDARD CONDITIONS

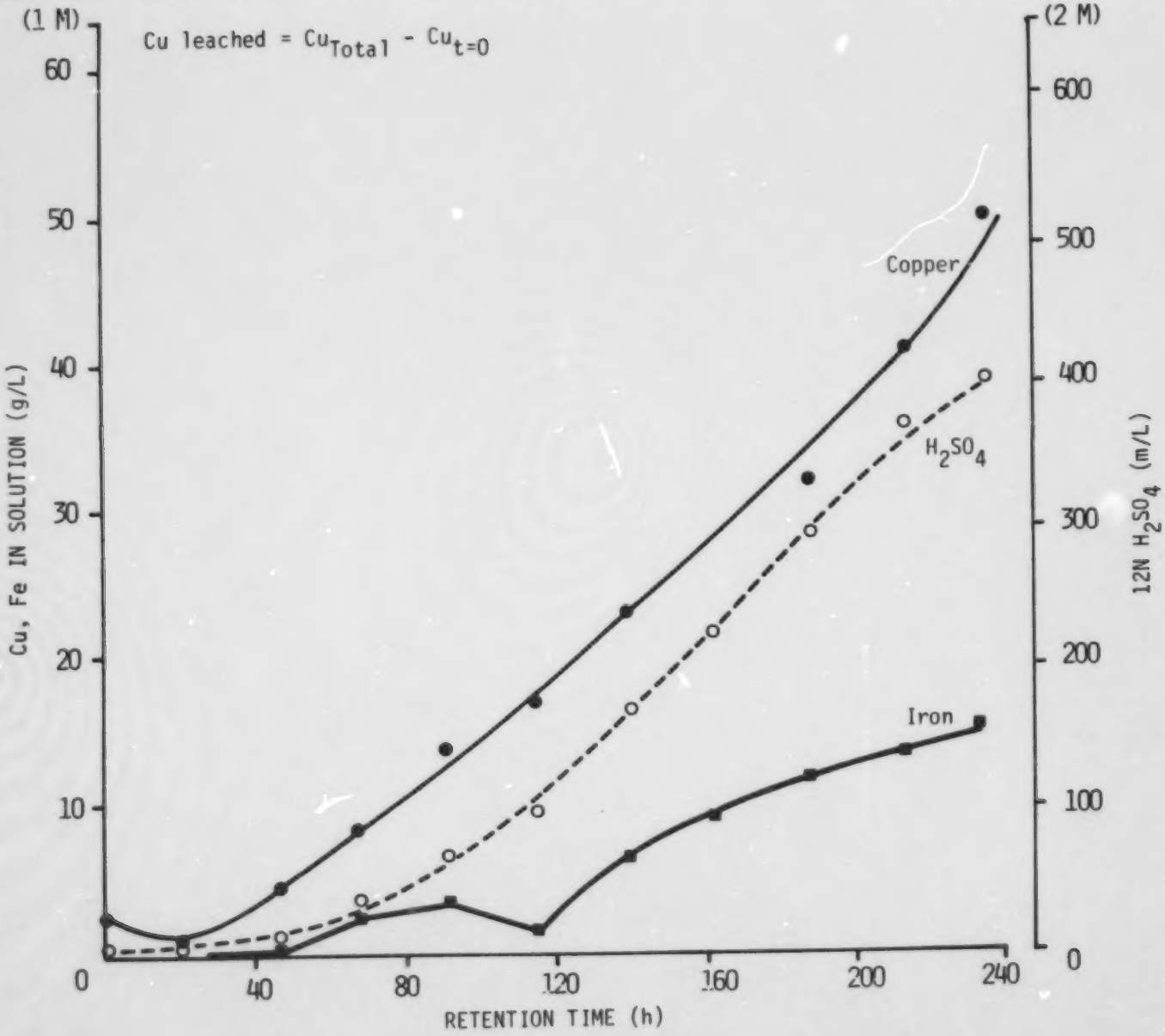


FIGURE 4

CATALYZED BIOLEACH OF GIBRALTAR CONCENTRATE (AS-RECEIVED) UNDER STANDARD CONDITIONS

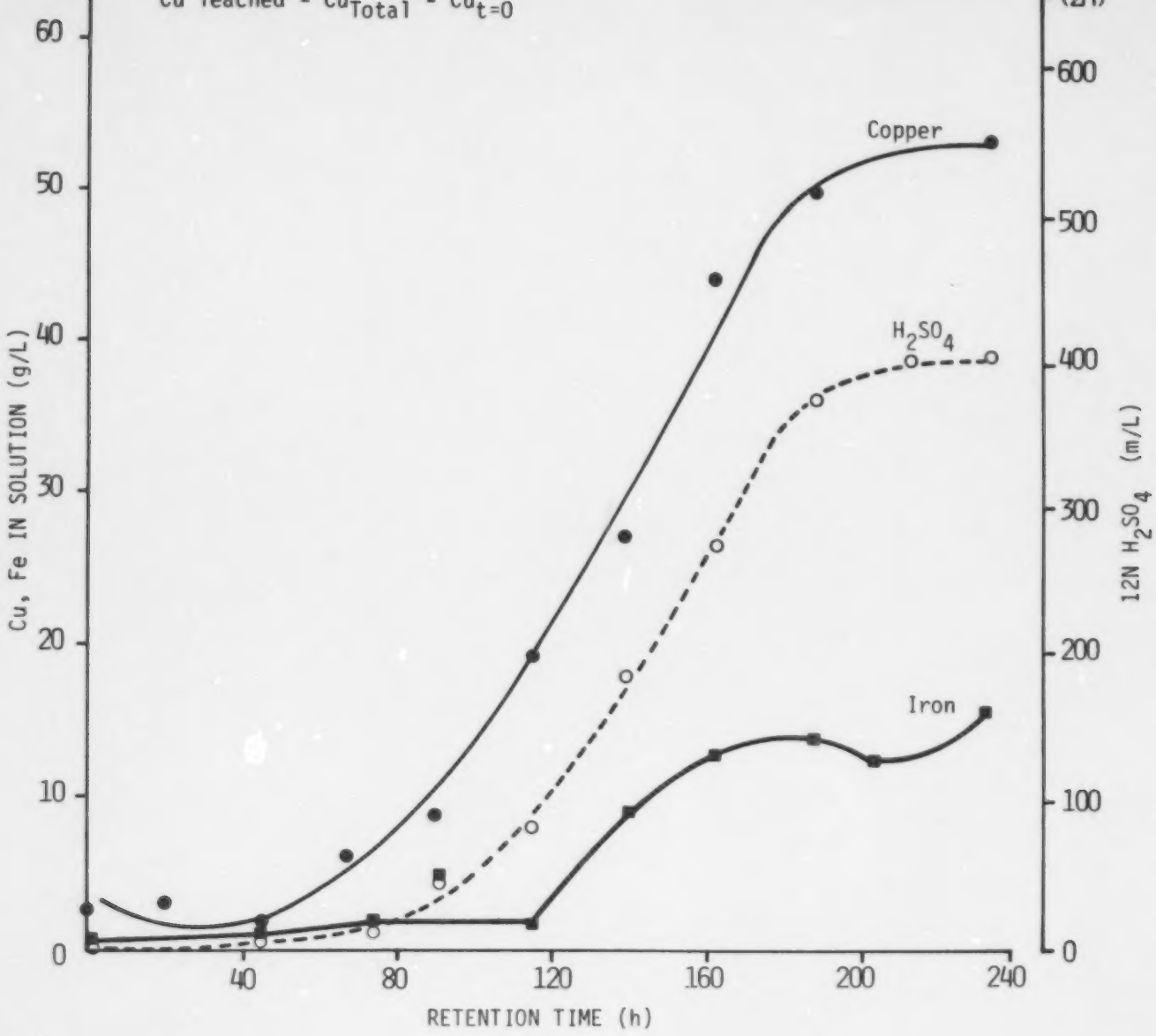


FIGURE 5

CATALYZED BIOLEACH OF GIBRALTAR CONCENTRATE (REGROUND) UNDER STANDARD CONDITIONS

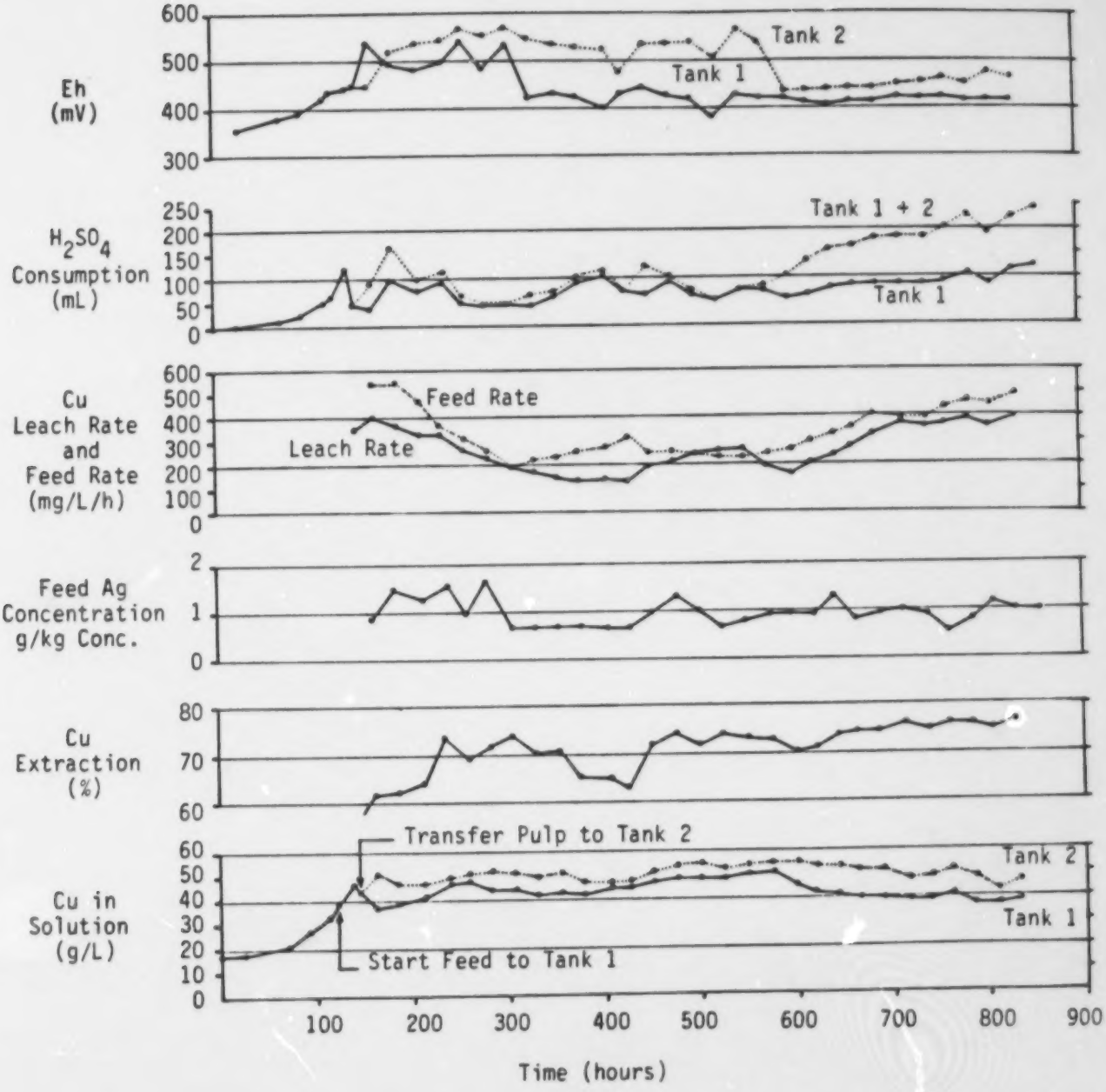


FIGURE 6

CONTINUOUS BIOLEACH OF GIBRALTAR CONCENTRATE

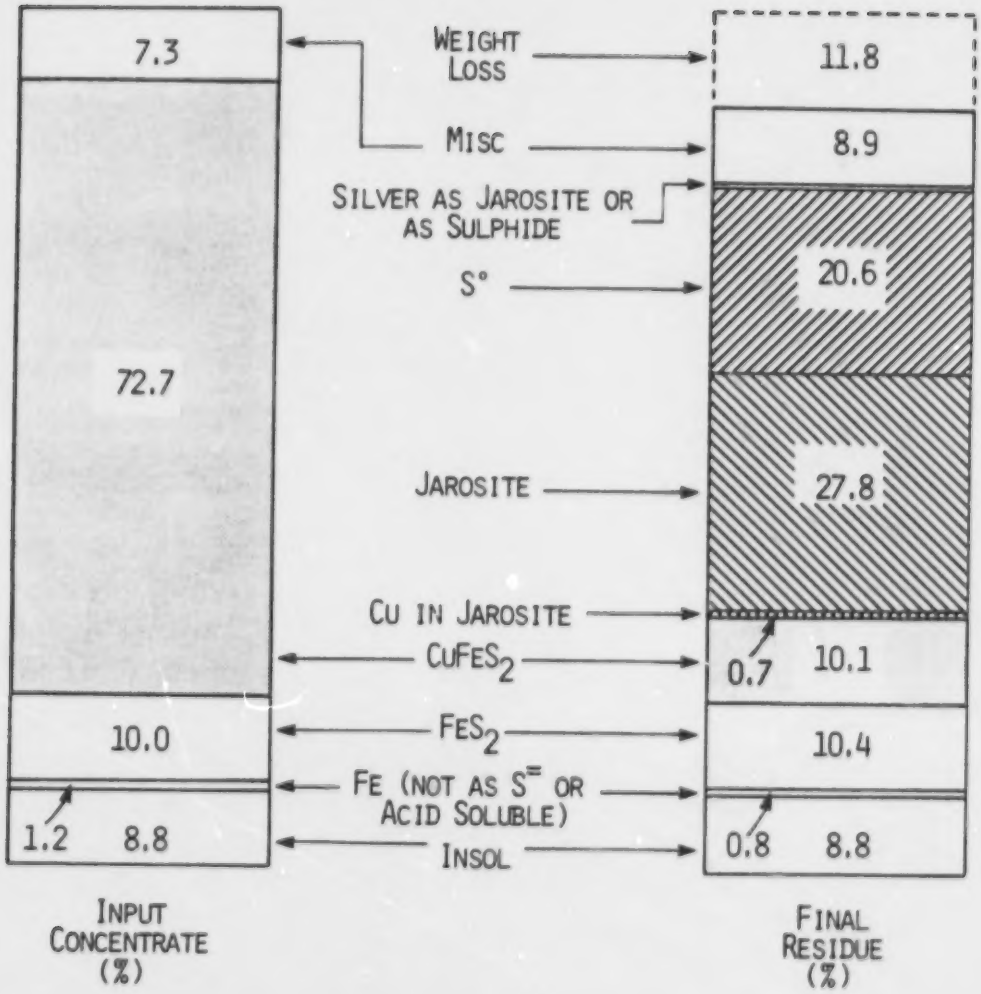


FIGURE 7

COMPARISON OF THE COMPOSITION OF INPUT CONCENTRATE AND FINAL RESIDUE

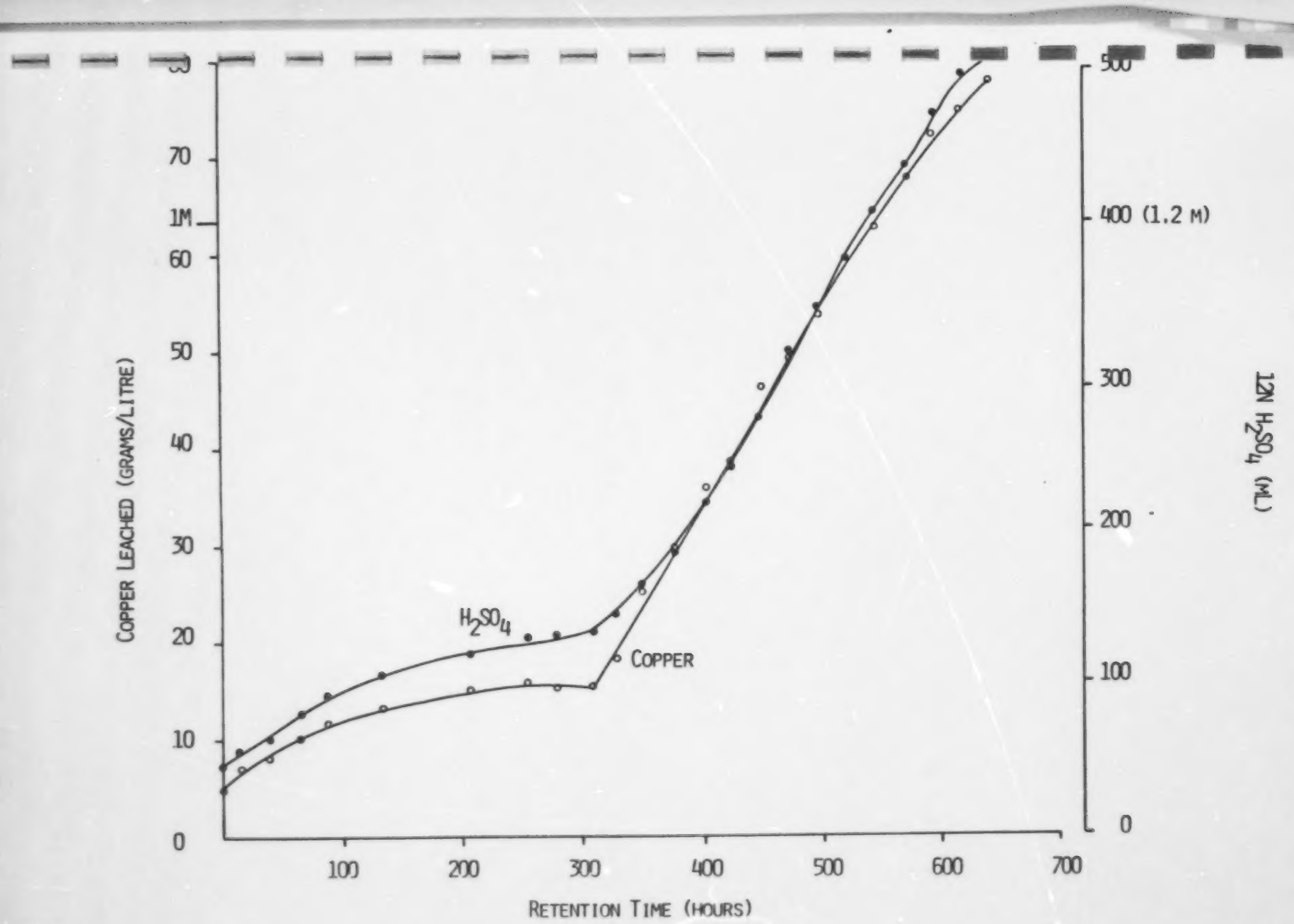


FIGURE 8

CATALYZED BIOLEACH OF WHITEHORSE CONCENTRATE

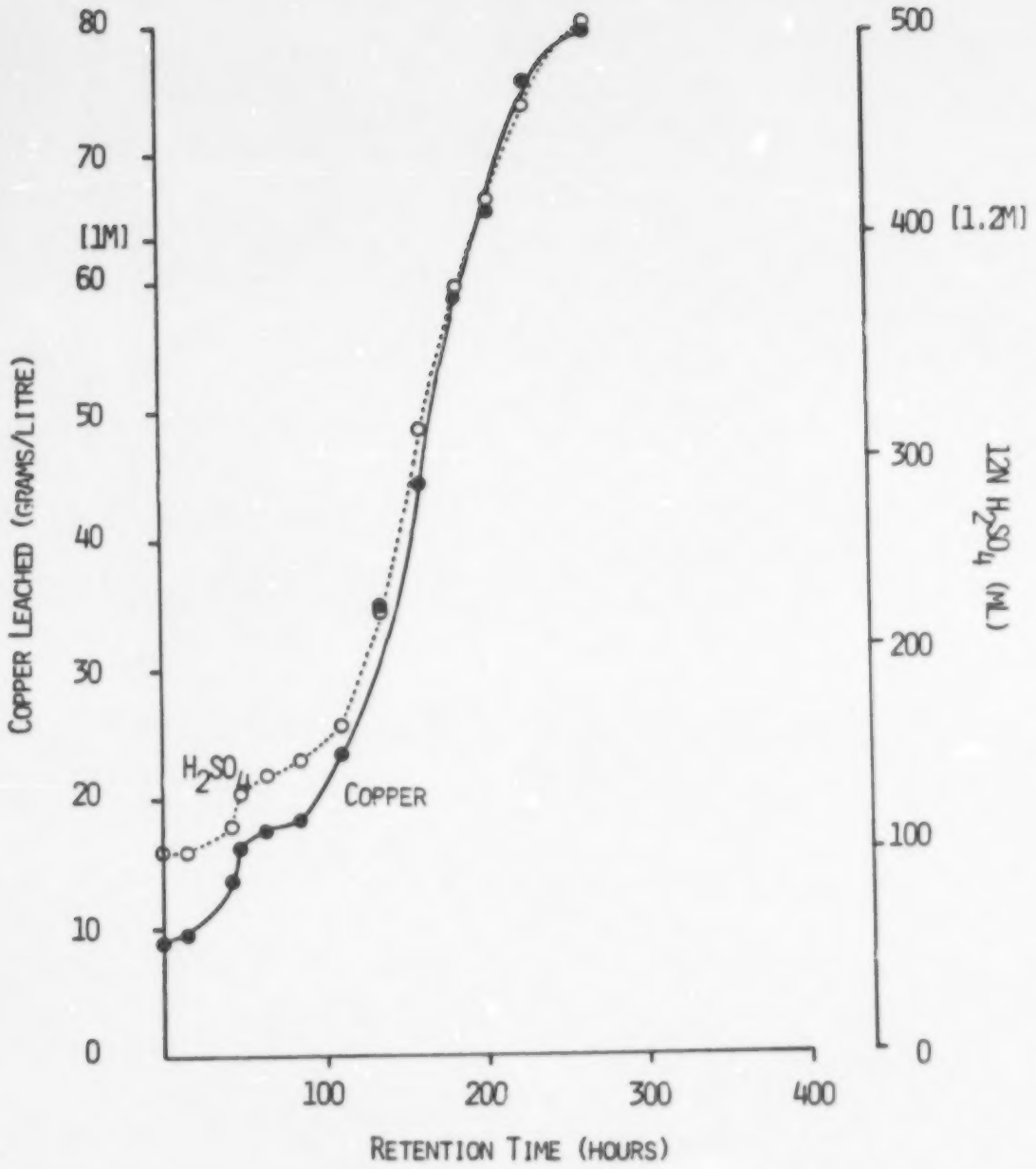


FIGURE 9

CATALYZED BIOLEACH OF ACID PRETREATED
WHITEHORSE CONCENTRATE

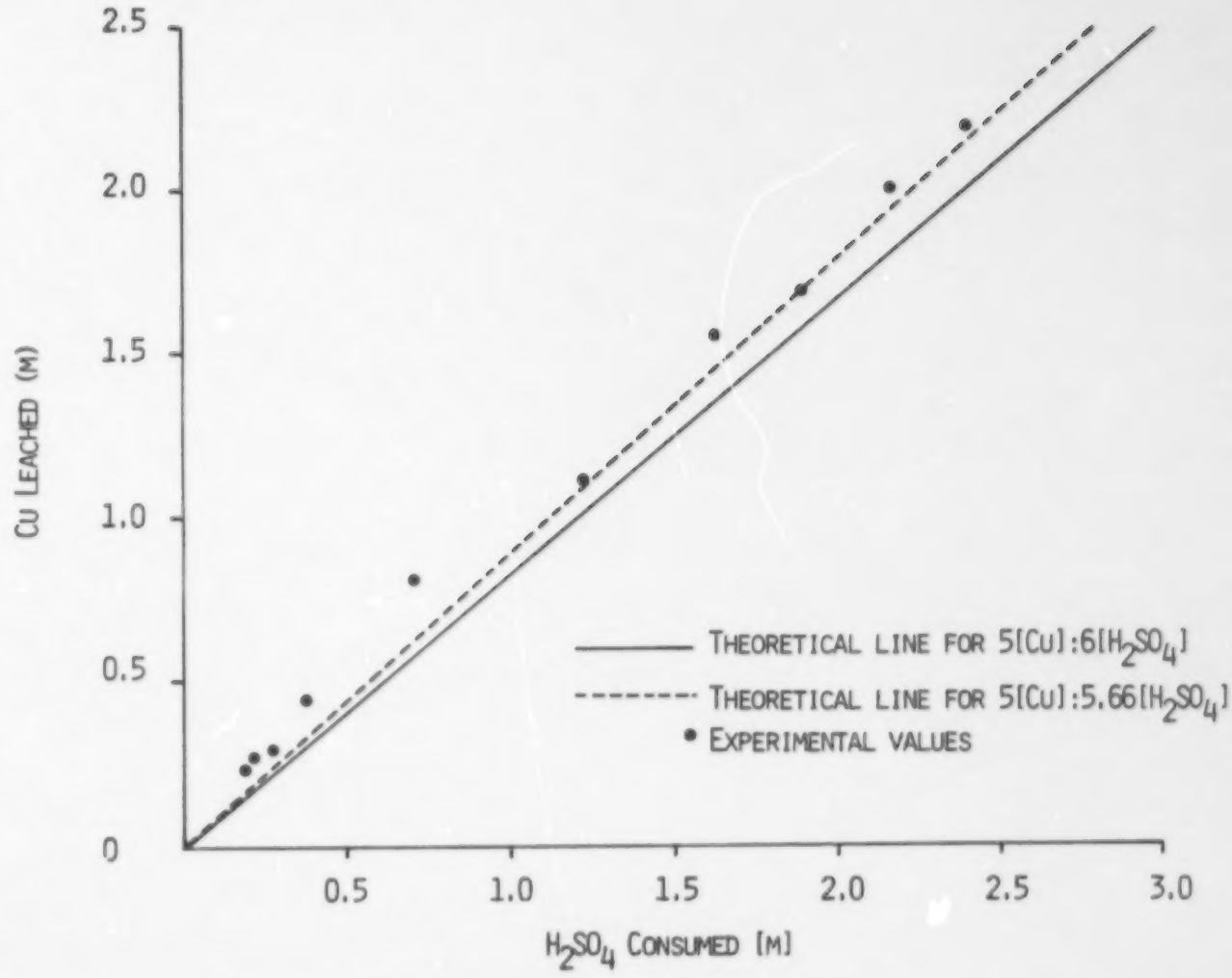


FIGURE 10

Cu:H_2SO_4 MOL RATIO FOR CATALYZED

BIOLEACH OF WHITEHORSE CONCENTRATE

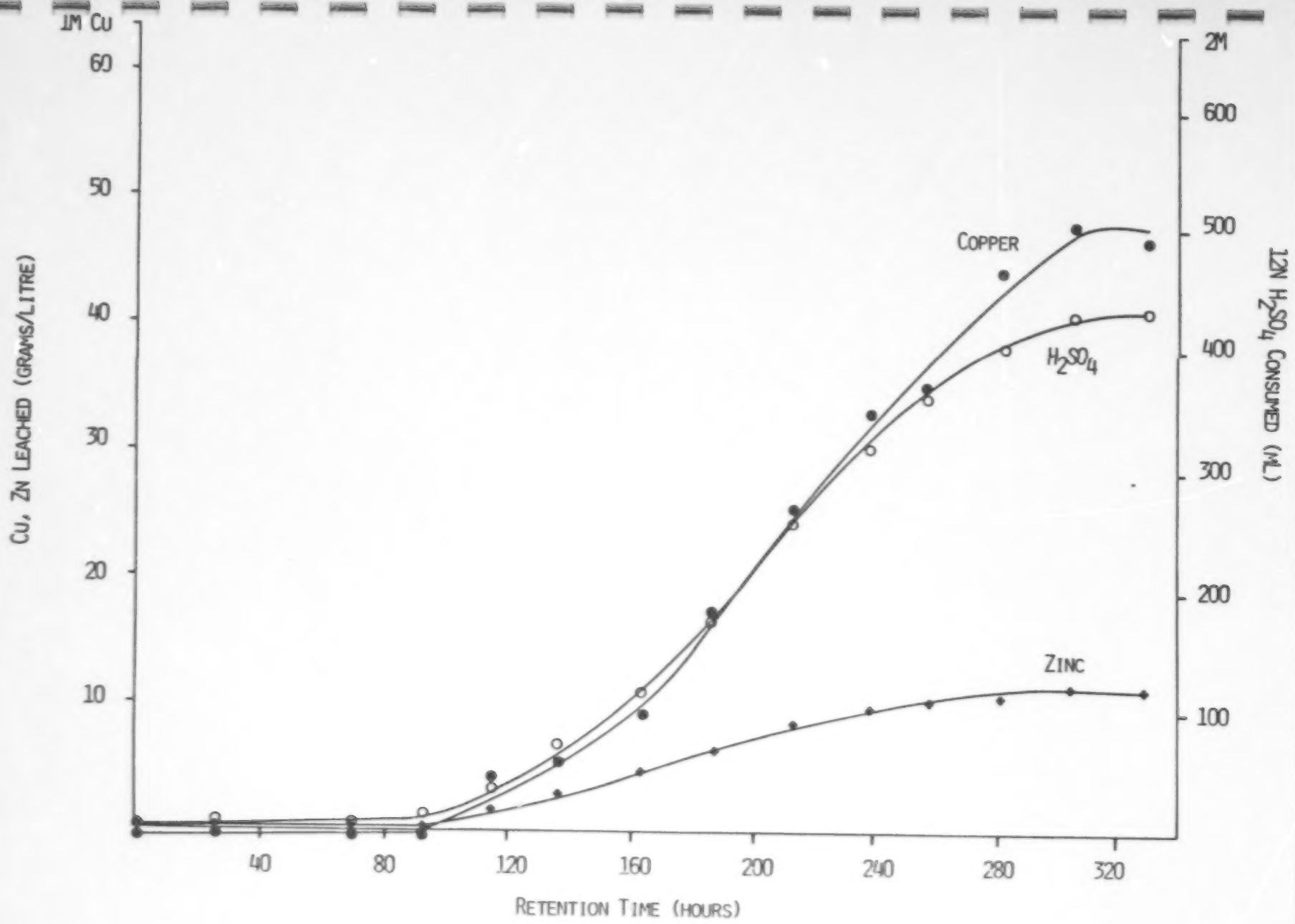


FIGURE 11

CATALYZED BIOLEACH OF SELBAIE CONCENTRATE

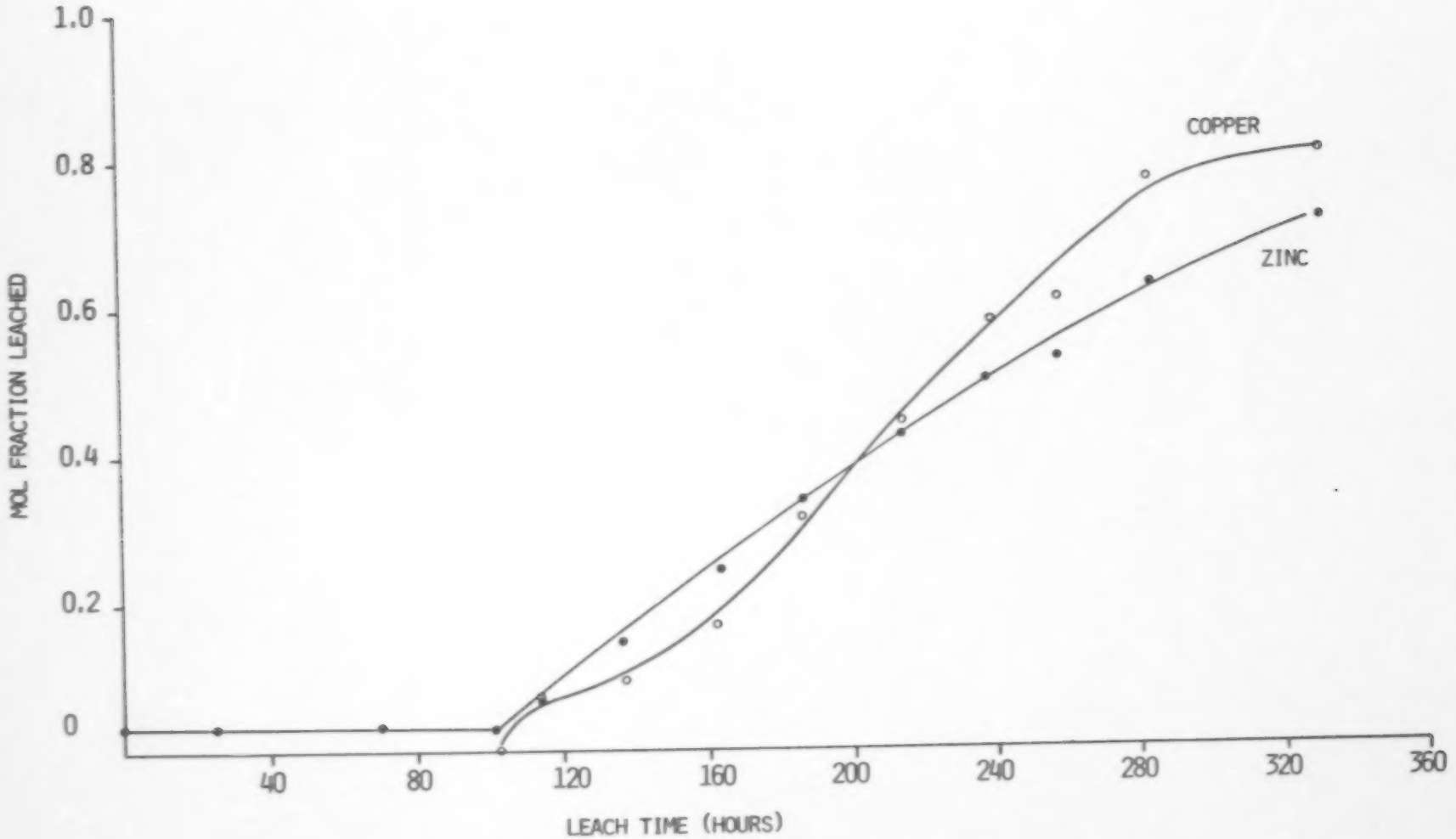


FIGURE 12

MOL FRACTIONS OF COPPER AND ZINC LEACHED IN CATALYZED
BIOLEACH OF SELBAIE CONCENTRATE

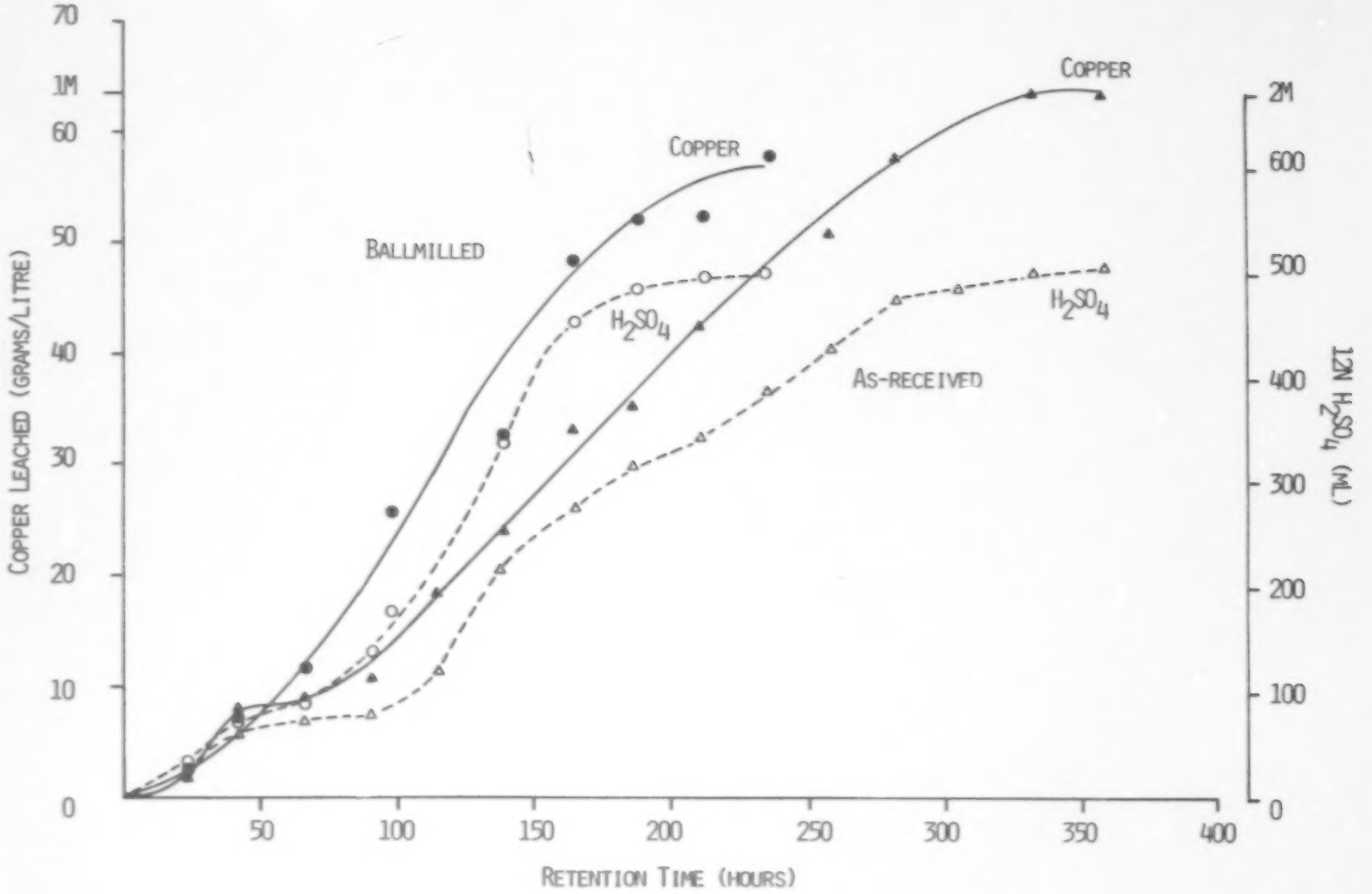


FIGURE 13

CATALYZED BIOLEACH OF SUMITOMO C CONCENTRATE: AS-RECEIVED AND BALLMILLED

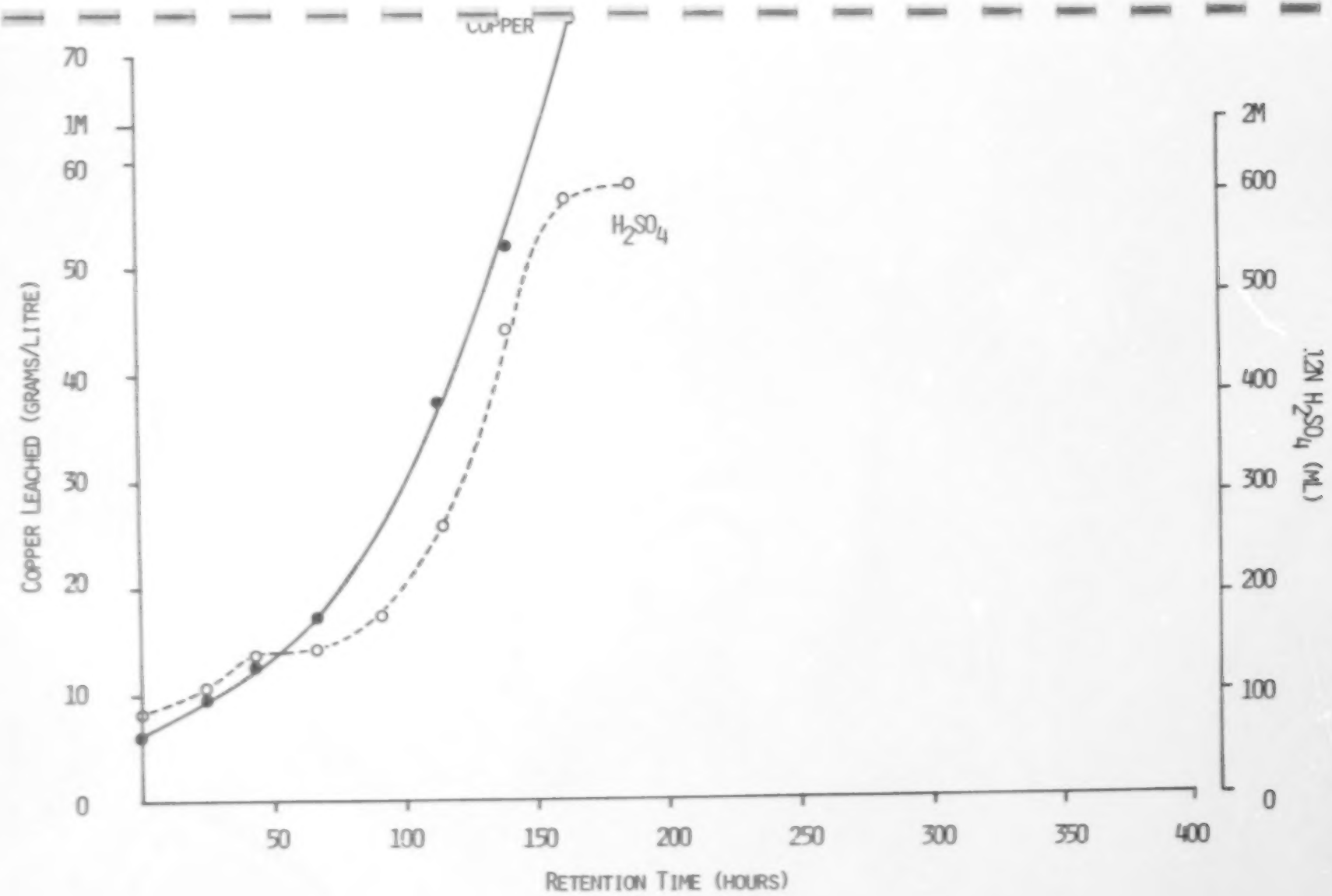


FIGURE 14

CATALYZED BIOLEACH OF PRETREATED SUMITOMO C CONCENTRATE (TEST #145)

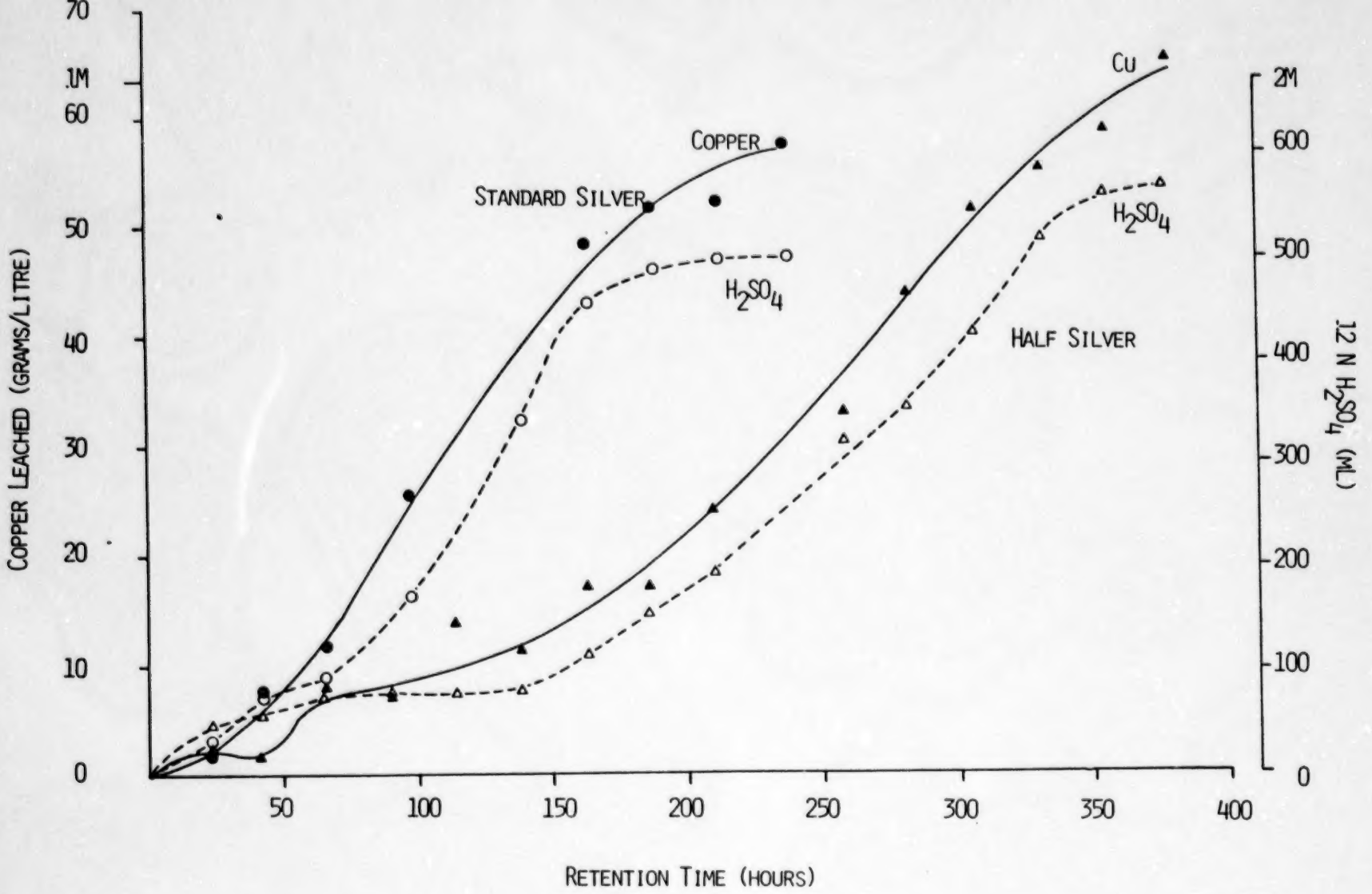


FIGURE 15

CATALYZED BIOLEACH OF BALLMILLED SUMITOMO C CONCENTRATE: STANDARD AND HALF SILVER ADDITION

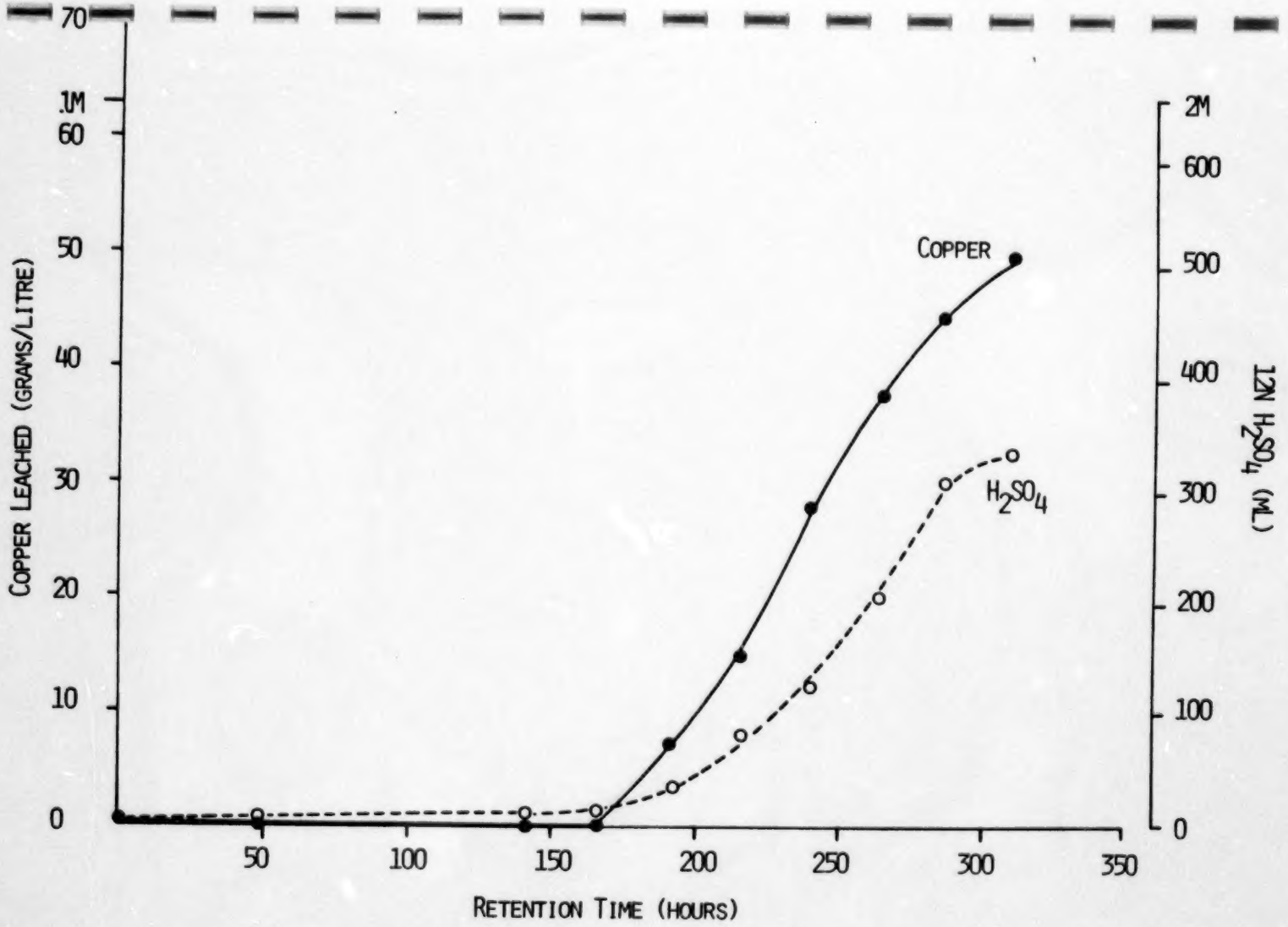


FIGURE 16

CATALYZED BIOLEACH OF MAGMA CONCENTRATE

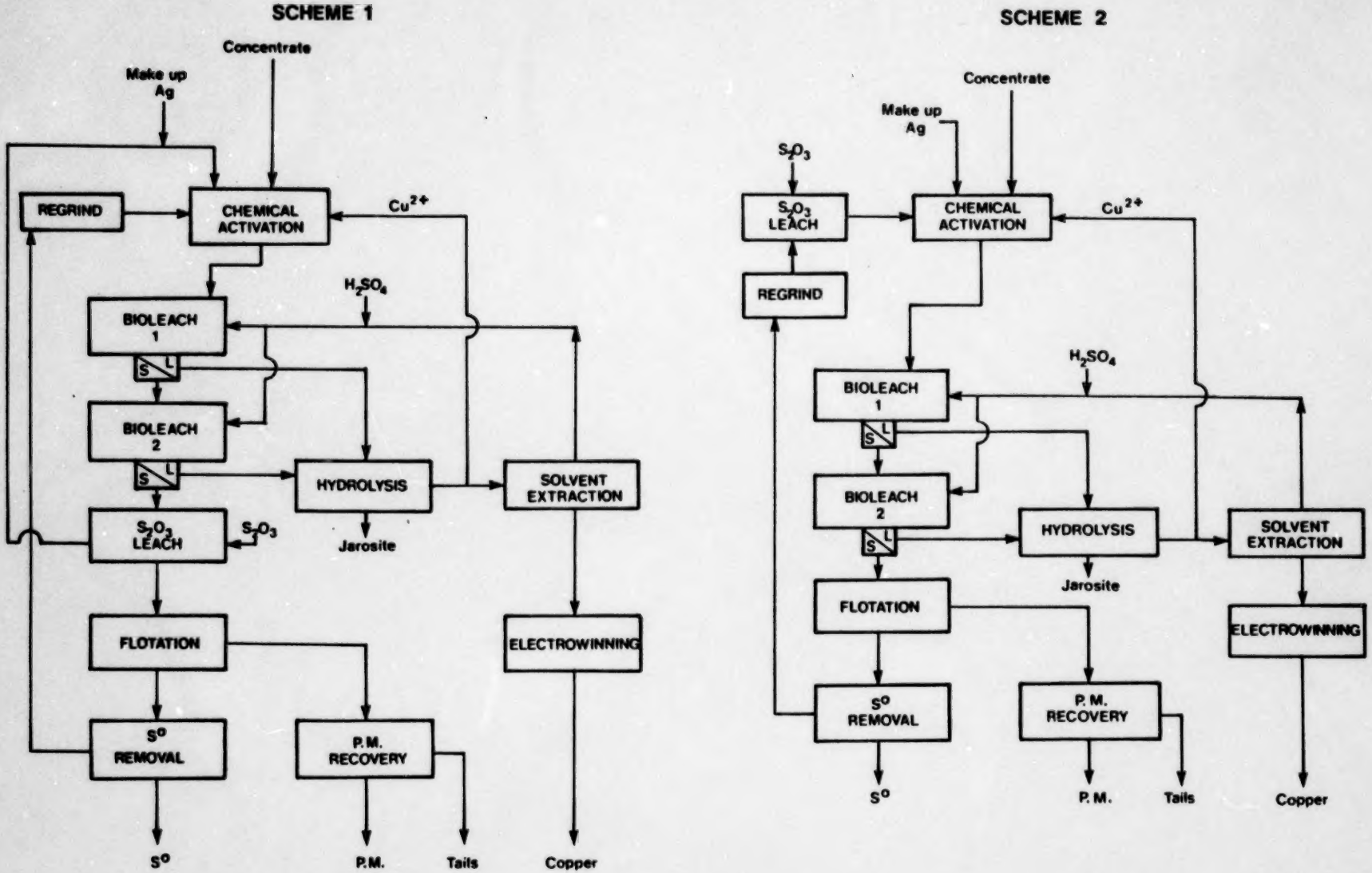


FIGURE 17

SILVER CATALYZED BIOLEACH FLOWSHEET SCHEMES